Chrysotype Manual:

Science and Practice of Photographic Printing in Nanoparticle Gold

Chrysonomicon Part II

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Preface

Throughout its entire history, up to the end of the 20th century, the practice of photography was governed by the photochemistry of silver halides. Their near-unique ability to record a latent image that is chemically developable provided the means for securing negatives almost instantaneously in a camera. Making positive prints from these negatives, however, is a more leisured business –exposures can be lengthy and light sources intense– so the door is also open to a whole range of non-silver *printing* processes, much slower than the bromide enlarging papers of the commercial monoculture. The so-called 'alternative' photographic printing processes, such as platinotype, cyanotype, gum dichromate, and carbon transfer, were supported by industrial products in the 19th and early 20th century, but the pressure of competition with the silver-gelatin medium has since declared them commercially non-viable. They are now relegated to the minority of specialist enthusiasts, who hand-coat their own printing papers with the light-sensitive chemicals.

During the early years of the 21st century, we have experienced a profound revolution in the technology of all the lens-based media. Silver halide photochemistry has been forced to abdicate its hegemony in favour of semiconductor photophysics: analogue chemical imaging has given way to digital optoelectronics, and the desktop computer has taken over from the 'wet' and sometime smelly darkroom. This revolution has immediately dematerialised all its photographic images: silver-gelatin negatives are replaced wholesale by digitally abstracted strings of binary code. Therefore the question still remains of how best to make the ultimate product that is humanly visible - the permanent photograph. For many purposes, the piezo ink-jet print serves well enough, but in the area of fine art and archival images, the alternative printing processes can still offer some unique, aesthetically satisfying, and permanent qualities.

Platinotype, once the preferred medium of many exhibiting 'art-photographers', has lately regained its status as a well-established minority practice. Together with its close homologue, palladiotype, it continues to justify the nineteenth century claim that this finest of processes is "simple, beautiful, and permanent". But the adjacent noble metal in the Periodic Table, gold, has never succeeded in gaining acceptance within the repertoire of photographic printing, apart from its use as a toning agent to stabilise and improve silver images. This was despite the early invention, by Sir John Herschel in 1842, of a pure gold printing process which he dubbed 'chrysotype'. However, the only gold salts known in Herschel's day were too reactive for the sensitizer, and had to be contained in a developer bath, which rapidly became contaminated, thus rendering the process totally uneconomic. Sporadic attempts to improve on Herschel's chrysotype met with little success, and by 1900 all the published authorities on photographic technology were unanimous in discounting the gold process *per se* as a photographic medium. Chrysotype then lay forgotten for over eighty years, until I revisited the problem armed with some knowledge of modern chemistry. By 1992 I had developed an economic working process,

comparable with platinotype in its qualities, which I simply called 'new chrysotype', in honour of Herschel's original invention.

Gold, as a pigment, has higher covering power than the other noble metals –a benefit which makes its use significantly less expensive than platinum or palladium. New chrysotype shares with its sister-processes, platinotype and palladiotype, the same characteristics of a totally matte print surface and a delicately nuanced tonal gradation. It also offers a valuable bonus: besides neutral grey tones, chrysotypes can be made in a wide range of subtly-muted colours, including pink, magenta, brown, purple, violet, blue or green. The creative monochrome photographer should find here an extra dimension to explore, in which the colour of an image can be matched to the expressive intent of its maker. The hue of the print is determined by the chemistry of the sensitizer and the conditions of processing, so the photographic artist has full control of this palette of non-literal colour. New chrysotype thus offers advantages in the beauty and permanence of its images –advantages that I hope may qualify it in the future as a unique medium of artistic photographic practice.

Prospective users of the new chrysotype gold-printing process should find all the practical information they need within this workshop manual. Much of its content is also relevant to the allied siderotype processes, platinotype and palladiotype, so it should interest the practitioners of these well-established printing techniques. This handbook provides the essential working information in a suitable format; it is complemented by my companion work: *Gold in Photography: the History and Art of Chrysotype*, which explores the historical, cultural, and aesthetic backgrounds to the uses of gold for image-making.

All the preparations, materials, and equipment needed for setting up an iron-based printing studio are listed and described in Chapter 1, with suggestions for sources of supply. An integral part of most hand-made photographs, especially chrysotypes, is the paper substrate, where the image resides in the surface fibres of the sheet and not in a binder layer coated upon it. Fine papers, their constitution and properties, are considered in Chapter 2, which lists the characteristics that are essential to their successful functioning with the siderotype processes. Chapter 3 provides some instruction in relevant chemical handling techniques and procedures, with due regard to issues of health, safety, and precision of measurement.

The core of this manual resides in Chapter 4, which publishes, for the first time, the full practical details for working three differing versions of my new chrysotype process, explaining their different characteristics and relative advantages. Other versions of chrysotype have also been developed, which offer further scope for modifying the appearance of the gold image, but they are not described here because their use could incur certain hazards that preclude their being published as methods recommended for the general public.

An essential prerequisite for the process is a negative having an appropriate optical density range; Chapter 5 therefore outlines several methods for the making of large negatives, including an introduction to the digital methods, using a desktop computer and ink-jet printer.

All the technical material that is not essential to the 'hands-on' practice is gathered into a set of appendices, which may be consulted for reference or educational purposes:

Appendix I provides a list of all the relevant chemicals in this work, their properties, and associated hazards, together with suppliers' catalogue numbers.

Appendix II describes some 'do it yourself' chemistry for experienced practical workers who prefer to prepare their own chemicals.

Appendix III provides reference tables for the conversion of the antique and obsolete units that may be encountered in the early literature, largely for the benefit of those interested in reinterpreting historical recipes.

Appendix IV carries an account of the chemical underpinnings of the process for those who are fluent in the language of reactions and molecular formulae.

Appendix V offers a quantitative treatment, for the mathematically inclined, of the factors influencing photochemical exposures for image-making.

Appendix VI is a glossary, intended to demystify any technical jargon unfamiliar to the general reader.

Mike Ware
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Preface to the revised digital edition

Since this Manual was first published in 2006, together with my book *Gold in Photography*, a number of practitioners have taken up the New Chrysotype process for making their own expressive work, assisted in some cases by workshops conducted by Gold Street Studios in Victoria, Australia. Prominent among these is Leanne McPhee who has been honoured with awards for her artistic work in the medium; her handbook of the process, *Chrysotype: A Contemporary Guide to Photographic Printing in Gold*, was published by Routledge in 2020, and is recommended for newcomers to alternative photographic printing in chrysotype. This book also includes a gallery of work by twelve contemporary artists in the chrysotype medium.

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1 Preparations for Iron-based Printing

This chapter describes all the facilities and equipment that are needed to hand-make photographic contact prints in nanoparticle gold. Although the topic of this monograph is specifically chrysotype, the general *modus operandi* presented here is also appropriate for the versions of the other iron-based alternative printing-out processes, or *siderotypes*,[1] such as I have published for platino-palladiotype,[2] argyrotype,[3] and new cyanotype.[4] The chemical recipes and procedures for these may also be found in my pages on the World Wide Web.[5]

1.1 The Working Environment

Your work surface for preparing sensitized paper should be clean, flat, smooth, dry, level, and at a suitable ergonomic height. You will also need a large wet-processing area, preferably a sink, to hold five photographic dishes of an appropriate size, together with a means for washing your prints in running water, and an indoor drying facility.

A secure cupboard is essential for the safe storage of all chemicals, to prevent access by children. The processing chemistry used here can develop a slight odour, so the workplace should be well ventilated. It is essential to observe clean working methods: any spilt substances must be removed immediately; remember that the sensitizer will stain most surfaces and fabrics rather strongly.

In the interests of consistent results, it is desirable to maintain a steady temperature in the work environment, between 18 and 24 Celsius (64 and 75 Fahrenheit), and preferably around 20°C (68°F). However, it is not essential to install air conditioning for the entire work space, because the relative humidity (RH) of the sensitized paper can be controlled locally by placing it in hydration boxes of known RH, as will be described below.

1.2 Ambient Lighting

The low sensitivity to light of iron-based alternative printing papers like chrysotype has a practical benefit: you do not need to work in a blacked-out photographic darkroom, equipped with special safe-lighting. Ordinary curtains or blinds should eliminate daylight sufficiently, and for preference the working area should be illuminated by a normal domestic light-bulb (incandescent tungsten or LED): a low wattage rating, distant two meters or more from the sensitive material and chemicals, is safe for the working time periods normally involved. A light switch with dimmer control may also be found useful. Avoid using light fixtures with fluorescent tubes; some types of these have a significant output of ultraviolet light which may cause fogging of the sensitized paper in time. Having set up your illumination, it is as well at some stage to perform a ‘safe-light test’ under the working conditions, as follows:

1.3 Safe-Light Test

- Lightly expose a piece of chrysotype paper (or other sensitive iron-based paper, such as new cyanotype) to your UV source. Give it an exposure that will be sufficient to bring it to a perceptible tone, but do not process it yet.

- Cut the sheet into several pieces and place them under the ambient working light with part of each area covered by a totally opaque object, such as a coin or one edge masked by metal foil.

- Remove and process one piece of paper after 10 minutes, then succeeding sheets at appropriate time intervals up to one or two hours. Alternatively you can perform a stepped test strip at appropriate time intervals of about 10 minutes, by sliding the sheet out of an opaque envelope.

- If, after processing, the 'shadow' of the coin or foil edge is visible it will give a measure of the degree of 'unsafety' of the lighting within a known time. Partially exposed paper is preferable to totally unexposed paper for this test because it is more sensitive to change, the fogging exposure having surmounted the 'toe' of the characteristic curve.

It is useful to maintain a completely dark enclosure somewhere in your work area, such as a cupboard or drawer, where sensitized papers can be kept for some hours or more while drying on racks or lines; it should be possible for the air to circulate freely through this enclosure and exchange with the environment, to avoid any buildup of humidity. It is also wise to store your light-sensitive chemicals in a dark cupboard or box, even though they are contained in amber glass bottles; this minimizes their long-term exposure to light and should increase their shelf-life to years.

1.4 List of Materials and Equipment

Pencils (soft 2B and hard 2H)
Ruler
Adhesive drafting tape (low tack)
Blower or brush for dusting-off negatives and paper
Spirit level (small)
White blotting paper
Sheet of plate glass (4 – 6 mm thick and larger than the paper)
Large clips (preferably plastic 'bag clips')
Jug to measure 1 litre (1000 cm^3) and stirrer
Storage bottles (at least 2) for processing solutions (1 to 2 litre)
Small graduated syringes, 1 and 2 cm^3 (at least 6);
Small mixing glass (a liqueur or 'shot' glass is ideal)
Brown bottles (3 or 4) for sensitizer solutions (ca. 50-100 cm^3)
Photographic dishes (5) – larger than the paper
Means of print washing, preferably in tray or dish
Timer
Contact-printing frame – see below
Ultraviolet light source – see below
Suitable negatives –see below
Sheets of artists' paper suitable for coating*
Glass spreader rods for coating the paper*
Chambers for controlled hydration of coated paper*
*The specifications for these three items are described in chapter 2.

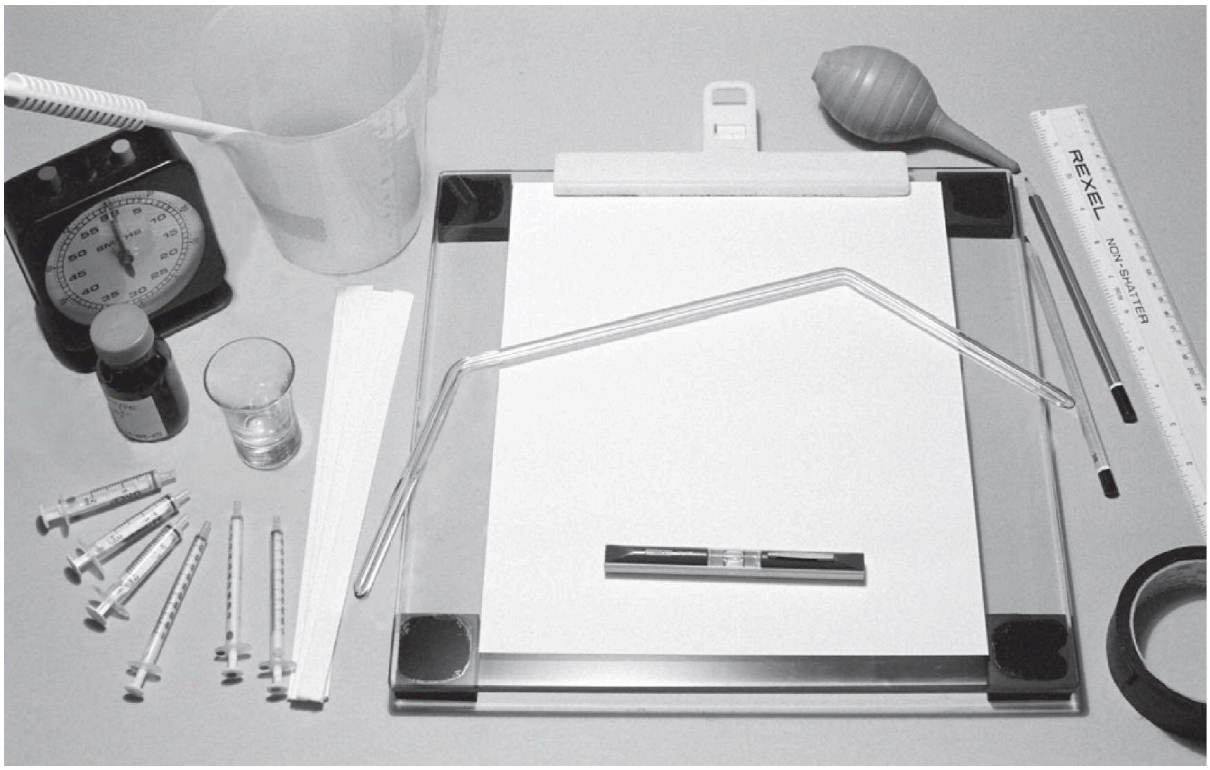


Figure 1.1 Typical equipment for coating paper.

The following items of chemical laboratory equipment will also be needed for making up the sensitizer solutions, as in Chapter 4 (figure 1.2):

A thermostatted hotplate/magnetic stirrer (ideally – or a hot water bath)
Scales accurate to 0.1 g and capacity at least 100 g – e.g. Salters' Model 1250 (or a chemical balance)
One glass measuring cylinder (‘graduate’: USA) 50 – 100 cm^3 capacity
Two Pyrex™ or Corning™ glass beakers 150 – 200 cm^3 capacity
Two glass stirring rods
One plastic beaker or jug or large measuring cylinder, 500 cm^3 capacity
Thermometer (0–110 °C)
Small spatula or plastic measuring spoon
Small conical filter funnel 5 – 6 cm diameter
Filter papers to fit funnel: Whatman Grade #1, 8 – 10 cm diameter
A washbottle filled with pure water
A supply of brown glass bottles with plastic screw caps, 50 cm^3 capacity
Self-adhesive labels for the bottles and an indelible pen

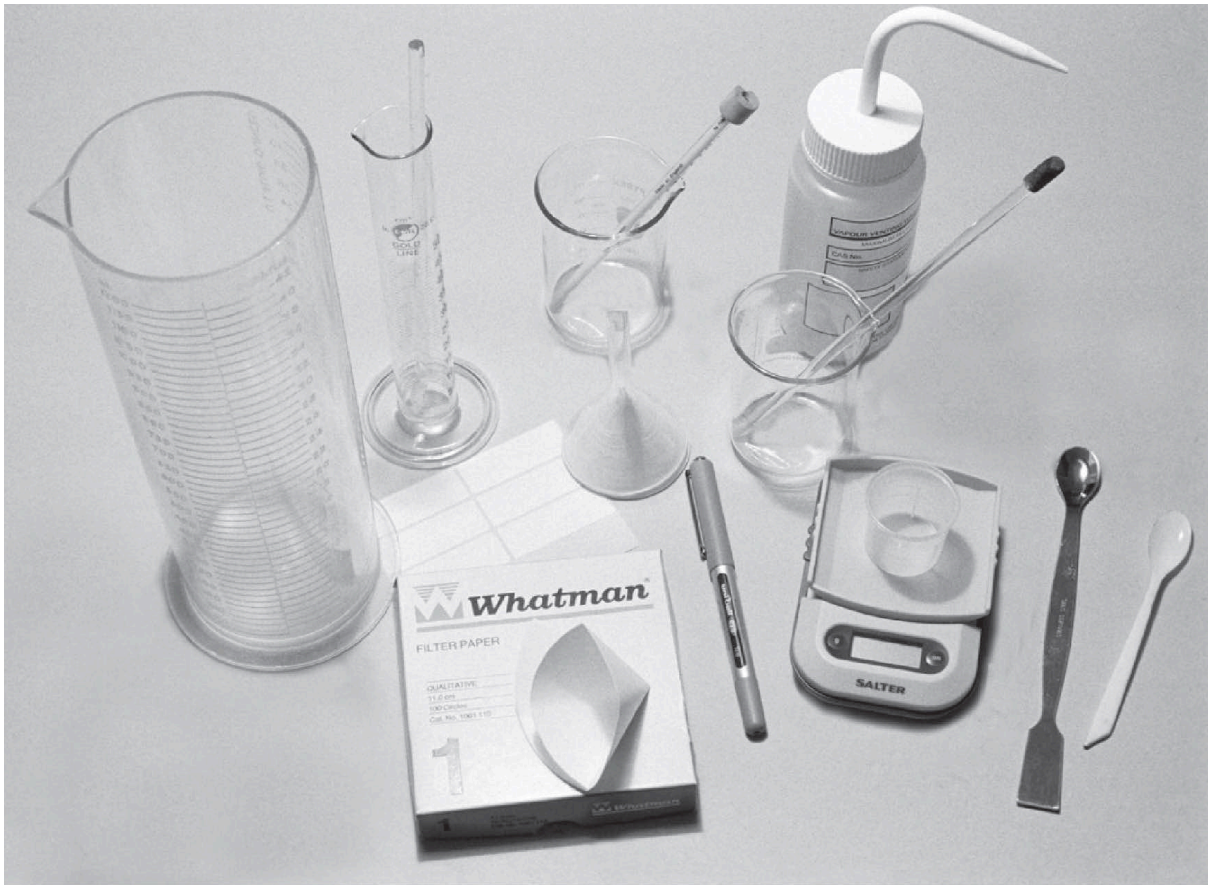


Figure 1.2 Apparatus and glassware for making up stock solutions.

1.5 Contact-Printing Frames

Some form of glazed frame is essential for applying enough pressure to maintain close contact between negative and sensitized paper surface. The simplest option is a sheet of plate glass 4 to 6 mm thick and a flat wooden baseboard with a thin sheet of foam rubber or felt as a backing to take up unevenness. Do not use 2 mm thick 'picture' glass, which may bend or crack under the pressure; and be sure to avoid the special UV-absorbing glass (it has been done!). This sandwich is held together by strong clips (figure 1.3).

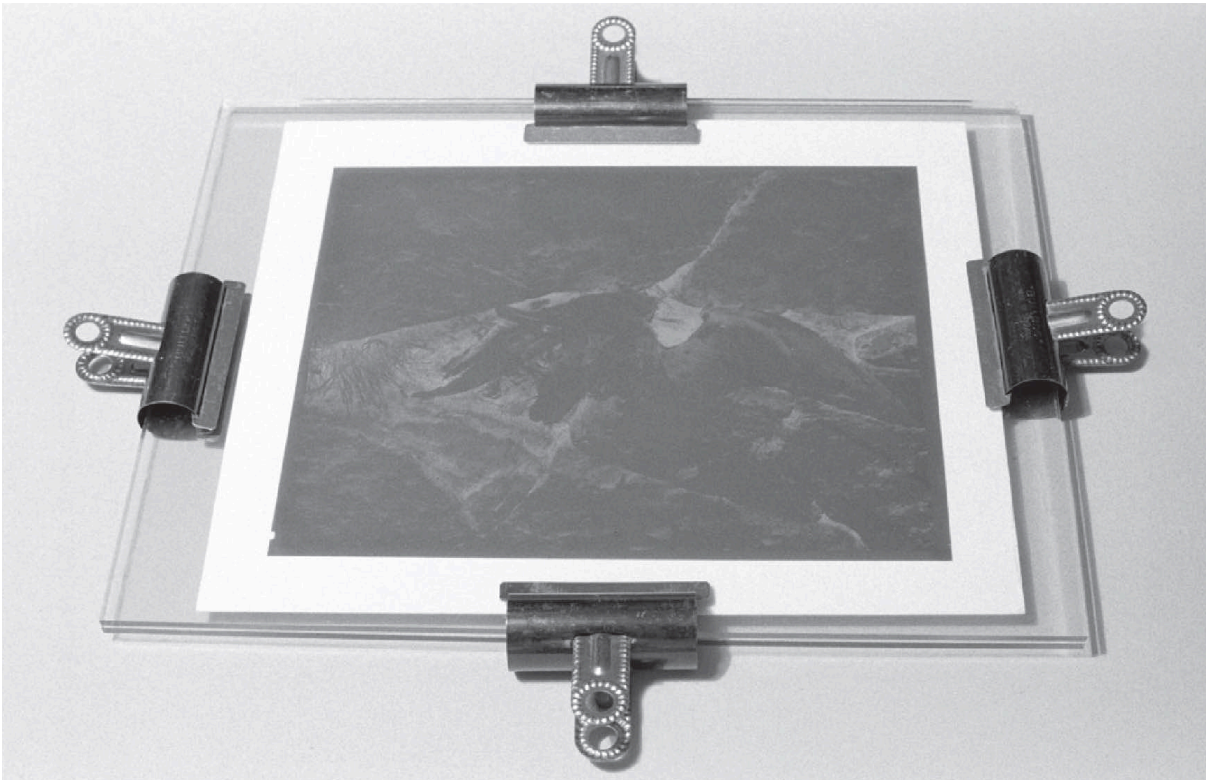


Figure 1.3. A simple printing setup.

Alternatively, one of the commercial contact-printing frames for proofing negatives may be used.

The chrysotype process, in most of its variations, yields a substantially printed-out image; that is, a fully detailed image is formed during the exposure, but subsequent processing will modify the appearance of this. It is therefore a great advantage to be able to inspect the progress of the printing (away from the UV source!) without losing the accurate registration between negative and print. This can be achieved with a hinged-back printing frame of the traditional design common in the nineteenth century, when printing-out was the standard practice. These can still be bought from specialist suppliers, and modern versions are often of high craftsmanship (and cost), but it is easy to construct a servicable version from a strong commercial picture frame kit of extruded, mitred aluminium alloy with a deep rebate to allow fixing of hinges (figure 1.4).

It is very important to include a sheet of papermakers felt sandwiched between the paper and the hinged pressure back to act as a vapour absorber for the CO_2 that is always evolved during the exposure;[6] this should be

slightly spongy to take up unevennesses, and larger than the sensitized area. It must not be stuck to the hinged back and divided into two, otherwise diffusion of gas or moisture through the hinged joint may cause a mark down the print, or modify the colour in undesirable ways. Plastazote™, a black plastic foam sheet, of archival quality, is another possible material.

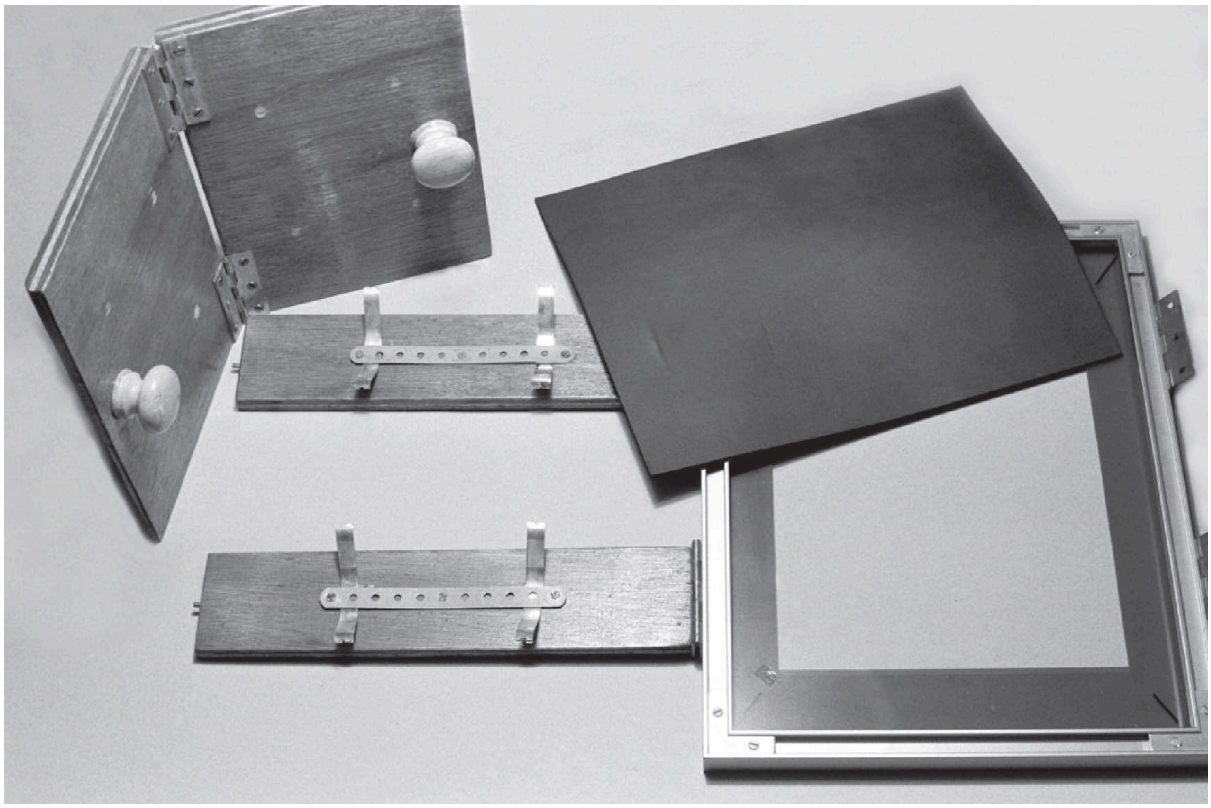


Figure 1.4. A hinged-back printing frame.

The glass interior of the printing frame shoould be masked with a window of ruby-lith, or other thin self-adhesive film that is opaque to UV and blue light (figure 1.4). This will impart clean, sharp edges to your images and a white border around them, rather than the overexposed borders which some workers consider fashionable. The popular practice of 'showing the brushmarks' to prove it's a handmade print is quite disadvantageous. Several glass windows may be so masked for the different formats you commonly use. Simply sticking the masking film on the front of the glass is not recommended: diffuse edges will be produced in the image. Apart from the issue of print aesthetics, masking the printing area confers three benefits:

- It avoids the generation, in the wet processing, of large quantities of redundant (non-image) pigment (in our case nanoparticle gold) in the exposed borders, which may bleed into, and stain the picture area.
- Exposed borders will also generate an unnecessary extra volume of CO_2 gas, which will contribute to the possible degradation of the image acutance if the gas cannot escape, but becomes trapped as bubbles betwenn negative and sensitized surface.
- The unexposed but coated borders of the print provide a valuable tell-tale check on the effectiveness of your clearing chemistry, as evidenced by the removal from this area of all traces of chemical stain,

compared with the paper margins. If you do not mask your negative when printing, but expose the entire coated area, then you will never know for certain if the print has been properly cleared.

Ordinary pressure-frame design is inadequate for very large contact prints, which demand more sophisticated technology such as a vacuum easel, but this precludes the possibility of inspecting the progress of the print during exposure, unless the negative is taped (at two points) to the underlying sheet, or the easel is fitted with registration pins. Care must be taken that the application of the vacuum does not change the humidity of the sensitized paper, by 'pumping off' the water during the exposure; once again a vapour absorbing sheet of felt is needed.

In contact printing there is always a risk that the sensitizer chemicals may damage the negative, which will be particularly vulnerable if the paper has been very fully humidified. In such a case it is always safest to use a duplicate negative. However, precious negatives may be protected during contact printing by interposing a very thin, uncreased sheet of archival polyester film - such as Mylar™ or Melinex™ - between paper and negative. If the plastic protective sheet is too thick, such a sandwich will, of course, diminish the edge sharpness or acutance of the print, and some resolution in the image may be lost, depending on the size of the light source. The degree of blurring may be calculated by a simple consideration of an idealised geometry of image formation, as follows: we shall assume that we require a circle of confusion in the image of diameter equal to the limit of resolution of the unaided human eye at its near-point - approximately 0.1 mm (100 μm).[7] If a diffuse light-bed of fluorescent tubes (say 600 mm long) is used at a close distance (say 60 mm), this suggests that the protective film should ideally be no thicker than 10 μm. In practice, I have found that with a film of 20 μm plastic the degradation of sharpness was imperceptible, even under a lens, but a plastic film of 50 μm thickness caused a 'softening' of the edges that was visible under close inspection; this was using a 'light bed' of fluorescent tubes. If a small light source at greater distance is used, e.g. the sun or a high-pressure mercury or metal halide lamp, then the more robust protective film of thickness 50 to 100 μm can be tolerated before diffusion of the image becomes perceptible.

1.6 Ultraviolet Light Sources

Any light source with a substantial ultraviolet content will serve for printing the iron-based processes, including chrysotype. However, incandescent sources like 'sun-guns' and quartz-halogen tungsten lamps and the sun itself also emit much infrared radiation, which has the undesirable effect of heating the sensitized paper as the exposure proceeds, so affecting the humidity and consequently the colour of the image. The preferred source is therefore a 'cold' discharge tube containing mercury vapour, and usually coated with an appropriate fluorescer.

The near UV portion of the spectrum is conventionally divided into three regions, referred to as UVA, UVB, and UVC; (below 200nm is the so-called 'vacuum' ultraviolet, which is substantially absorbed by air). There is no advantage, and much additional risk, in employing the more dangerous

'short wave' ultraviolet mercury lamps emitting UVB and UVC which rapidly damage eyes and living tissue.

Type	Wavelength Range nm	UV line nm[8]	Absorption	Damage/Hazard
UVA	400-315	Hg 365	skin	Tanning of melanin Can cause melanoma
UVB	315-280	Hg 313 Hg 297	partly by ozone windowglass proteins 270-290	Causes sunburn (erythema)
UVC	280-200	Hg 254	DNA 260-270	Lethal to organisms

Table 1.1. Conventional regions of the UV portion of the spectrum.

Long wave UVA lamps emitting chiefly a wavelength range of 315-400 nm (nanometers) are manufactured in several designs for graphic arts purposes such as diazo and screen printing, as well as for domestic sun-tanning or attracting insects. The most convenient and efficient sources are fluorescer-coated mercury discharge tubes, having a maximum output centred on a wavelength around 350-370 nm, close to one of the principal emission lines in the mercury atomic spectrum at 365 nm. See Appendix V

To ensure stable running from a normal mains supply, all mercury discharge lamps in their usual form require 'control gear': a circuit combination of capacitors and wire-wound chokes, which are heavy due to their metal laminations. However, there are now available high frequency electronic systems of control gear, which are much lighter, and tend to provide more lumens per watt; these are worth seeking out, despite the added expense, for ease in constructing the light box.

In Europe, one of the major manufacturers of UV fluorescent tubes is Phillips plc, whose designations for suitable lamps are: actinic /05 (peaking at 370 nm) or actinic /09 (peaking at 355 nm). These are available in various lengths and power ratings, but are usually in the order of 10-20 watts. In the USA the tubes made by Sylvania, called 350BL have the desired emission, as do the BL tubes of General Electric. Users in the USA should note that the manufacturers' designation 'BL' indicates a suitable tube; this stands for 'black light' - even though these sources do also emit much visible light. The US designation 'BLB' stands for 'black light blue', as in the General Electric BLB tube, and signifies tubes that are fitted with a deep blue glass envelope that filters out almost all the visible light, transmitting only a band of UV around 350 nm. While these may create a desirable ambiance in a discotheque, and they do perform quite acceptably for print-making, their use is not advantageous, either in efficiency of light output or greater cost.

Metal halide lamps are physically much smaller than the fluorescent tubes and have to be used at a greater distance to achieve uniformity of illumination. They therefore have to run at much greater power (typically 1000 watts or more) to deliver the same flux of UV at the print. Their only advantage is that, being more nearly point sources, the acutance of the print is higher, especially if there is a plastic film intervening between negative

and paper. Their disadvantage is the need for a 'warm up period' during which the output is not constant, so exposures cannot simply be timed unless the lamp is left on continuously, but must be measured with a light integrator, which accumulates a measurement of the total dose of light.

Fluorescent lamps are also marketed, called 'Super-Actinic' (SA) or 'Aqua' (these are intended for aquarium use), with a peak output in the blue, around 420 nm (this corresponds with the Phillips spectral designation: actinic /03) and these have found favour with some workers. Such lamps are not, however, very efficient for cyanotype or platino-palladiotype (despite claims to the contrary), where the internal filter effect is strong at this wavelength (see Appendix V),[9] so while they may work well enough with chrysotype, or kallitype, they are not the best choice if you also intend to use the other iron processes. The standard SA tube does have the advantage of being nearly four times as powerful (75 W instead of 20W) which compensates somewhat for its lower actinic efficiency. See Appendix V for a detailed treatment of the wavelength sensitivity of iron-based sensitizers.

Comparative tests have been made of the several kinds of lamp available in the USA: types BL, BLB, SA, and mercury-metal halide (HID), using several alternative processes, including some siderotypes.[10] Under the same conditions, the differences in printing speed between the various UVA lamps were not found to be great, or dependent on the manufacturer: for the same power rating, usually four tubes of 20 watts each, the exposures needed to produce the maximum density were found to differ only by half a stop or less. However, the contrast produced by the various lamps in a given process did appear to vary more widely, as measured by the logarithmic exposure range from D_{max} to paper white. The most potent factor affecting the emissivity of lamps is simply old age.

The following UV sources are listed in approximate ascending order of cost:

The sun. This is of course free, and pleasant to employ, but it is an uncertain and variable source in most locations that are not blessed with a perfect climate. The sun is effectively a point source, subtending an angle of half a degree of arc (0.01 radians), consequently giving high acutance. It is about four times (2 stops) faster than a typical commercial source such as a diazo printer. There is a significant heating effect, however, which may affect the colour of the print and the ease of clearing the excess chemicals. The clear blue summer sky is a totally diffuse source about 3 stops slower than the sun's direct UV intensity. The apparent relative angular motion of the sun of 15°/hour (i.e. it moves through its own apparent diameter in 2 minutes) is not a serious consideration for printing, unless the object (diaphane or negative) is not in contact with the paper; in which case exposures longer than one or two minutes can result in blurred edges to the shadows.

A Pifco 300 watt UV lamp No. 1012 (figure 1.5)***.*** These small domestic sunlamps can still sometimes be purchased cheaply from second-hand sales, especially when the public has been recently reminded of the dangers of melanoma. They should be used at a distance of about 30 to 50 cm from the printing frame to achieve uniformity of illumination over the print, and will be rather slow in printing.

Mercury discharge reprographic lamps, such as the Philips HPR 125W (figure 1.6). These should used at a distance of about 30 cm from the frame, or at a greater distance if an array is employed to cover a large area. They are high pressure mercury arcs, contained in an outer glass envelope fitted with a standard ES connection. They require the usual mercury discharge control gear for the ballast, and are commonly employed in commercial 'plate burners' and 'screen-printers' for the graphic arts.

Figure 1.5. Pifco 300 W UV lamp.

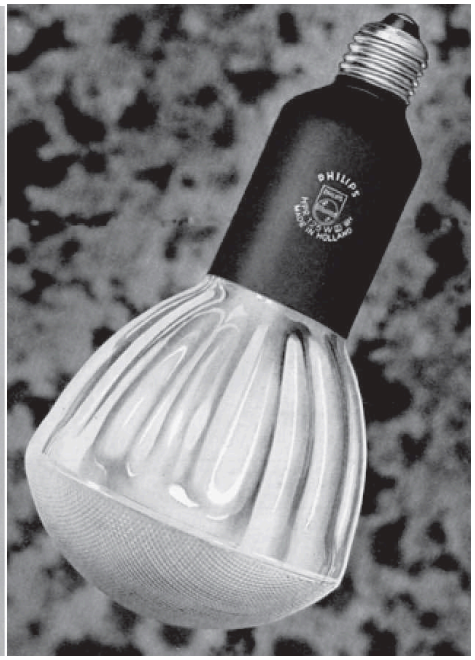


Figure 1.6. Philips HPR 125 W.

A 'facial' or 'half-body' solarium (figure 1.7)***.*** The so-called 'facial solarium' is a small, inexpensive version of the domestic UV suntan bed, and is particularly recommended for prints of modest size. The Philips "Decolleté Half Body Solarium", uses 6 Philips "Cleo" UVA tubes (actinic/09) 400 mm long, with a power of 20 W each, and is an efficient self-contained unit, at a moderate price, which can be used for prints up to 30 x 35 cm.

Figure 1.7. Philips Facial Solarium 120 W.

A commercial luminaire, fitted with UVA tubes (figure 1.8)***.*** Lighting equipment suppliers sell such ready-made housings for arrays of fluorescent tubes, equipped with all the sockets and control gear to take four 600 mm, (24”) or larger, fluorescent tubes mounted in a metal case, which may be provided with reflectors. The plastic diffusers are not required.

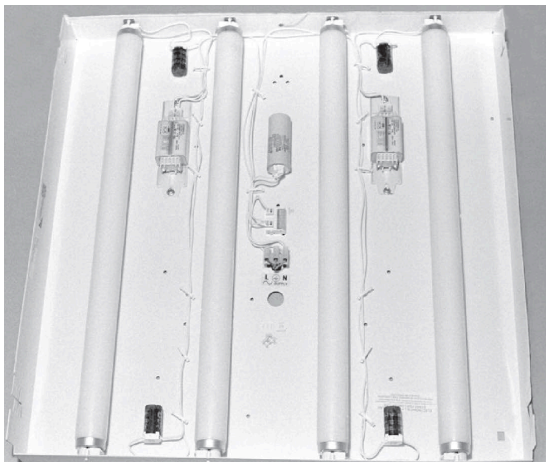


Figure 1.8. Commercial luminaire.

A Diazo printer (figure 1.9). This is convenient unit, once marketed by Gordon Audio-Visual for the now obsolete diazo process. It provides a ‘light bed’ of four Philips fluorescent tubes, type TLADK 30W/05 UV, distant 8 cm from the print, and accomodates an image up to 25 x 30 cm (8 x 10 in).

Figure 1.9. Gordon Diazo-printer 120 W.

A domestic suntan bed. These emit UVA, and are useful for very large prints or a workshop situation where multiple printing is going on.
A NuArc printer. This is a commercial UV exposure system, with a small high intensity mercury or metal halide lamp, and a vacuum easel. It is also equipped with a light integrator. It is manufactured for the graphic arts and screen printing industry, and can be recommended for alternative printing when high cost is no obstacle.

1.7 Geometry of Illumination

Two aspects of the geometry of light sources for printing deserve comment. First, the question of the optimum distance between the light source and the sensitive surface. Placing the printing frame close to the light source increases non-uniformity of illumination and the degree of heating; but increasing the distance between them leads to light loss and longer exposures. To optimise performance, we need an answer to the question: how does the light intensity fall off with distance? It is well-known that the intensity of illumination from a point source falls off as the inverse square of the distance[11], but it would be a mistake to suppose that this applies to an extended 'light bed' of fluorescent tubes; we must look at the other theoretical results. From an infinite line source (approximated by a single tube), it may be proved that the intensity falls off inversely as the distance, but if the source is an infinite 2-dimensional plane (a 'light bed'), the intensity does not fall off at all with increasing distance! In practice, of course, no real source is infinite in extent. The relationship between intensity and vertical distance from the plane of the source is therefore dependent on the dimensions of the source: the mathematics is easiest to do for a circular disc, radius R.[12] At a perpendicular distance H from the centre of the disc it can be shown that the illuminance falls off according to the mathematical function:

$$1/(1+ (H/R)^2)$$

this function is conveniently tabulated against the ratio H/R:

H/R	1/10	1/8	1/4	1/2	1	2	4	8	10	
$\frac{1}{(1+ (H/R)^2)}$	$\frac{100}{101}$	$\frac{64}{65}$	$\frac{16}{17}$	$\frac{4}{5}$	$\frac{1}{2}$	$\frac{1}{5}$	$\frac{1}{17}$	$\frac{1}{65}$	$\frac{1}{101}$	
% illumination	99	98.5	94	80	50	20	6	1.5	1	%

Table 1.2 Varying illumination with distance for a disc-like 'light bed'.

In practical terms, from these figures we can see that the loss of light with increasing distance is small when the print is distant less than half the radius of the light bed (for H/R = 1/2, loss = 20%). At a distance equal to the radius, (H/R = 1) the illuminance is halved (50%) and we have 'lost one stop' of exposure intensity. As the ratio H/R increases further, the behaviour begins to come into conformity with the familiar inverse square law, as we would expect. Although our light beds are rectangular, rather than circular, this theoretical result is a sufficient indication for practical purposes, without going into the more complicated mathematics of a rectangular source.

The separation between the fluorescent tubes in a light bed array is also important to the uniformity of illumination at the printing surface; when the tube separation is too large compared with the distance to the print surface, "barring" or "banding" of the print will occur, due to parallel regions where the light intensity is greater. However, it is surprising how widely the tubes

can be spaced before this effect actually becomes perceptible. It is certainly unnecessary to pack the tubes as closely as possible, which is an unconsidered feature of many designs for light boxes, and a more generous spacing of them will improve both cooling and accessibility. Calculations suggest that a tube spacing comparable with the vertical distance from tube to print surface should not give rise to perceptible "barring", and this is born out in experimental tests.[13] There are directions for the construction of light boxes in Nadeau's treatise,[14] the *Journal of Post-Factory Photography*,[15] and Stevens book *Making Kallitypes*.[16]

Whichever source you use, you must configure it so that there is no risk of direct radiation entering your eyes. If this proves impossible, be sure to protect your eyes with appropriate UV-absorbing goggles, such as those supplied for domestic sun-tanning. The World Health Organization has recommended that the total short period exposure of skin or eyes to UVA should not exceed a total dose of 10^4 J/m^2 (Joules per square meter), this corresponds to an energy density of 10 W/m^2 (Watts per square meter) for a period of 1000 seconds (approximately 16 minutes).[17] The Gordon diazo printer, which is a typical UVA source, delivers 50 W/m^2 at the glass platen, implying that the maximum permitted eye-exposure to this source is about 3 minutes. Even so, I would not recommend staring at it!

Compared with the relatively low biological hazard presented by UVA,[18] radiations in the UVB and UVC regions are intrinsically far more dangerous because they are absorbed by proteins and DNA around 270 nm, and they destroy the visual pigments of the retina. The WHO Maximum Permissible Exposure limit to the unprotected eye (over a period of 8 hours) at this wavelength is only 30 J/m^2. This translates into about half a second's exposure to a source with an intensity of 50 W/m^2.

1.8 Characteristics of Negatives

There are many options open to the photographer for making large, continuous tone negatives; Chapter 5 discusses the various methods in detail, but a few general guidelines need to be stated at this stage. The basic requirement for iron-based printing is for a large negative (format 5"x4" or bigger) having a density range extending from the usual fb+f (filmbase plus fog) density of about 0.2 or less, to a D_{max} (maximum highlight density) in the order of 2.2 - 2.4. This is about twice the density range needed for normal silver-gelatin printing, and may usually be produced in a film by giving a normally-exposed camera negative about 80-100% extra development time, or by using a correspondingly more concentrated (about 2 x) developer. To be sure of not 'printing through' and degrading the 'whites' to grey, in the rebate of the negative and specular highlights, the film should be capable of a D_{max} of about 3 or more. Conventional black and white film, orthochromatic or panchromatic, is best for contact printing by UV. Colour negative and chromogenic films usually have UV-absorbing layers built into the sheet, so can be very slow to print through; for the same reason, Polaroid negative material may also be problematic.

1.9 Wet Processing Arrangements

The procedure for dish or tray processing is largely a matter of commonsense: slide the print smoothly, face up, under the surface of the processing solution; if the dish is held tilted away from you initially, a 'tidal wave' of solution can be allowed to wash back rapidly over the surface of the paper as the dish is restored back to the horizontal. Delays in total immersion can cause tide marks. Once the image is fully wetted, it must be carefully inspected for any surface air bubbles, which are removed with a soft sable brush. The paper sheet may then be carefully turned over, and the rest of the processing carried out face down, provided that it floats. This offers some protection against ambient light, but more importantly it ensures that the chemicals are more thoroughly diffused and diluted as they wash out; it also minimises the effects of 'bleeding', as excess chemicals or metal pigment fall away. It is also appropriate because plain paper sheets, unlike silver-gelatin papers, usually tend to float on the surface. For a few papers which are compacted or heavily sized, it may be found that they tend to sink to the bottom of the dish, in which case they should be processed face up for better diffusion of chemicals and to avoid abrading the image surface. When transfering the paper between baths, grip the sheet with tongs near the centre of the top edge, not by one corner, or it will be more liable to tear. Alternatively, wear gloves and hold the paper carefully with both hands at the top corners, without stressing it. Fine art papers are much less robust when wet than silver-gelatin photographic papers. To protect your skin, use tongs or wear gloves at least for the first two processing baths, where most of the residual chemicals accumulate. Only intermittant agitation, every minute or so, is necessary.

Washing is best done by keeping the prints horizontal, in trays, using a syphon; a cascade arrangement is useful if you are printing a run. Standard photographic print washers having vertical compartments can be problematic, because plain paper is more buoyant than silver-gelatin photographic papers. Try to establish a tempo in your exposure and processing intervals, so that the transfer of prints from one dish to the next can be synchronised, and indicated by a simple interval timer set to repeat every ten minutes.

1.10 Drying and Flattening Prints

Your drying facilities need be no more sophisticated than an indoor 'clothes-line' and plastic pegs; but you should select the design of your clothes-pegs very critically, choosing only those that can grip a thin sheet of paper reliably, but preferably without leaving any impression. A preliminary draining of the wet print for 10 minutes or so, adhered to a near vertical sheet of glass or perspex propped up in the sink, will save a lot of dripping of water. If the paper is gelatin sized, then blisters may be avoided by squeegeeing the print face down onto the sheet of perspex.

Air drying horizontally on racks covered with nylon mesh is preferable to pegging the sheets onto a line, especially if the paper is fragile, but such drying racks are expensive and occupy considerable space; it is also important that you keep the drying screens scrupulously clean.

Prints will dry substantially flat, without curling like fibre-based photographic papers, but they may develop some residual 'cockling' around the edges. They may easily be pressed totally flat, but should be separated between sheets of the finest white blotting paper, or preferably the conservation blotting paper Multisorb, or Whatman #1 filter paper. The prints should be at an RH above 75% at least, in order to relax the fibres: the 'compliance' of a paper sheet is much greater when still humid. You can apply the pressure with a letter-press or an unheated drymount press, or simply under flat boards and weights. Be careful of the alignment of one print over another to avoid overlapped edge marks being pressed into the paper. If high pressure is available, it is possible to press a 'platemark' into the sheet using a polished metal ferrotype sheet or even a thick Melinex or perspex sheet: this will tend to cold press a 'glaze' or 'burnish' onto the image, which will be visible as a sheen to the matt surface, but it may improve the density of the blacks slightly.

1.11 Finishing and Retouching Prints

When the print is thoroughly dry, remove any pencil guide-lines with a soft, high-quality eraser. Flaws may be retouched with the best quality artists' water colours - not Spot-tone dyes, which are intended for silver-gelatin, and which penetrate plain papers too deeply. Use a scrap of the same paper to test and match your colours before applying them to the print.

Titling, annotations of date and reference number, and your signature should be written in the margins of the actual print (not on the mat), using a hardish (2H) graphite pencil so they cannot readily be erased, and will leave an impression. It is possible to have an artists' 'blind stamp' made, which leaves a deeply embossed impression as an indelible identification of the origin and nature of the print (figure 1.10).

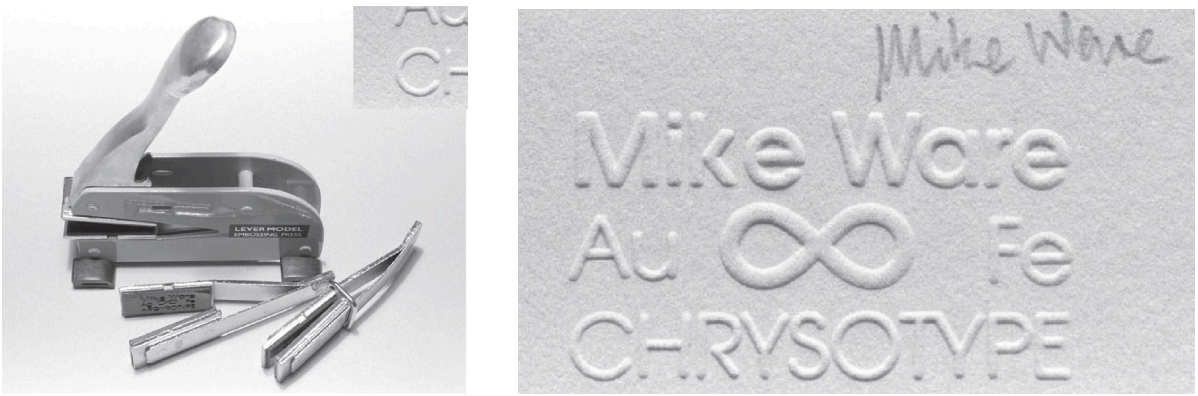


Figure 1.10. Embossing press and personal blind stamp.

1.12 Suppliers of Photo Equipment and Chemicals

The major fine chemical supply houses are listed in Appendix I

UK

Process Supplies (London) Ltd.
13-25 Mount Pleasant
London
WC1X 0AR
UK

Tel: +44 020 7837 2179
https://www.processuk.net

Silverprint Ltd
Unit 26 Albany Park
Cabot Lane
Poole
BH17 7BX
UK

Tel: +44 (0)1202 051 180
Email: sales@silverprint.co.uk
https://silverprint.co.uk

Continental Europe

Wolfgang Moersch Photochemie
Am Heideberg 48
50354 Hürth
Germany

Tel: +49 2233 943137
Fax: +49 2233 943138
Email: wolfgang@moersch-photochemie.de

Laboldtech2000
Via Europa n. 72/D11
20047 Cusago
Milano
Italy

Tel: +39 02 903 94213
Fax: +39 02 903 93715
https://www.laboldtech.eu

USA

Artcraft Chemicals Inc
PO Box 583
Shenectady
NY 12301
USA

Tel: +1 518 355 8700 or 800 682 1730
Fax: +1 518 355 9121
Email: artcraft@peoplepc.com
http://www.artcraftchemicals.com

Bostick & Sullivan
P O Box 16639
Santa Fe
NM 57506 – 6639
USA

Tel: +1 505 474 0890
Fax: +1 505 474 2857
Email: orderinfo@earthlink.net
http://www.bostick-sullivan.com/

Photographers' Formulary
PO Box 950 / 7079 Hwy 83 N
Condon
MT 59826
USA

Tel: +1 406 754 2891 or 800 922 5255
Fax: +1 406 754 2896
Email: formulary@blackfoot.net
http://stores.photoformulary.com/

AUSTRALIA

Gold Street Studios
700 James Lane
Trentham East
Victoria 3458
Australia

Tel: Ellie Young 613 5424 1835
Email: ellie@goldstreetstudios.com.au
https://www.goldstreetstudios.com.au

2 Choice and Coating of Paper

A correct choice of paper is crucial to the success of siderotype processes, especially chrysotype. Many newcomers to the practices of alternative printing make the optimistic assumption of expecting every ferric process to work on any old paper. They might just as well expect a process to work with any old chemical, because the paper is an integral part of the chemistry. With the iron-based processes, the sensitizer solution is imbibed into the surface fibres of the paper sheet where it comes into intimate chemical contact with the cellulose – and with every other substance that happens to be present in the paper, due to the manufacturing process: some of these substances may be hostile to the photochemistry. This situation is quite different from that pertaining to conventional silver-gelatin papers, or to the pigmented colloid-hardening processes, such as carbon transfer, where the paper sheet merely acts as an inert substrate, providing a physical support for, and being largely insulated from, the colloidal layer adhering to it, in which the image is formed. To aid the selection and purchase of papers for alternative siderotype printing, the reader will be introduced in this chapter to some of the technical terms and jargon from the language of the papermaker.

2.1 The Manufacture of Paper

The raw material for making paper is called the 'furnishings', and consists of plant tissues with a high cellulose content: cotton, flax, hemp, jute, esparto grass, hardwoods, or softwoods, and other more exotic sources of plant fibre. The structure of the cellulose fibres of these various plants differs widely and greatly influences their paper-making properties. Wood sources also contain up to 40% lignin,[19] which has highly undesirable properties for paper-making: it decomposes under the action of light, turning yellow and releasing acid.[20] The presence of any lignins in a paper will sooner or later cause a deterioration –seen as a discolouration and embrittlement as is encountered in newsprint, for example– and they should be totally avoided. In the manufacture of most papers, wood pulp is 'delignified' by chemical treatments at elevated temperature and pressure, either by acidic sulphites (the 'Sulphite' process), or by alkaline sulphides (the 'Kraft' or 'Sulphate' process) to solubilise the lignins; unfortunately these processes also degrade the carbohydrate to an extent, and such pulps are still discoloured by residual lignin so must be bleached before forming papers for printing and writing. Papers made from wood pulp, even delignified, are not generally reliable materials for siderotype.

The various methods and machinery for manufacturing paper are well-described in standard texts, which should be consulted for details.[21] The great majority of manufactured papers are not usable for siderotypes, so much of this technology is not relevant to us. The only satisfactory papers are to be found among those intended for the fine-art market –a tiny proportion of the total industrial production.

In manufacture, the cleaned plant fibres are first suspended in water and refined or beaten to a pulp by machines called Hollander Beaters –a process called fibrillation, which greatly increases the surface area by

shredding or teasing out the fibres and which enables better interlocking of the fibre network when the sheet is formed. Various chemical additives may be made to the 'vat' of pulp, known as 'stuff', at this stage, as will be discussed shortly. To form a sheet of paper, an appropriate volume of the pulp is drained down (sometimes assisted by vacuum) through a fine metal wire screen stretched over a rectangular wooden frame – the paper 'mould'. This mesh acts as a sieve or strainer to retain the cellulose as the water is drawn off, and the fibres are shaken sideways to help them interlink. This is the traditional skill of the 'vatman' in hand-making paper; the mould is then passed to the 'coucher' who turns the sheet out of the mould onto a stack, with alternated 'felts' to dry it under pressure in a pile called a 'post'.

The greater proportion of papers intended for fine art purposes are now machine-made, however, using a rotating cylindrical wire mould that dips into the vat of pulp, and is connected to vacuum; the continuous sheet is taken off –'couched'– onto a moving felt blanket, pressed and dried between rollers; such 'cylinder mould machines' run slowly to achieve a high quality sheet. The great bulk of papermaking, however, employs Fourdrinier machines, with a linear moving wire mould, which run at high speed and volume.

2.2 Characteristics of Papers

The properties of a sheet of paper that are most important to the alternative process printer will be considered next.

2.2.1 Furnishings

Purity and reproducibility in a paper are essential to the iron-based processes, so the only papers of serious interest to us are those made solely from cotton or linen, having a high (>98%) cellulose content. These are still sometimes called 'rag' papers, although recycled rags, once a major industry, are no longer used in their manufacture. For strength, it is desirable to select cotton with as long a fibre as possible. Papers made from a mixed furnish of cellulose fibres from different sources can absorb sensitizer unevenly, causing a fibrous granularity or blotchiness in the print, so should be avoided. The detailed chemistry of paper and its structure are considered further in Appendix IV. Pure cellulose papers, carefully processed, have the best expectations of archival permanence of any substrate for printing. Specimens of 'rag' paper made 500 years ago are still known in excellent condition. In contrast, mechanically ground woodpulp papers of only a few decades ago, e.g. newsprint, are already seriously advanced in decomposition.

2.2.2 Laid or wove moulds

Paper moulds are of two distinct kinds, depending on the pattern of interweaving of the metal wires: a 'laid' mould of close parallel wires, bound by more widely spaced 'chain' lines, leaves ribbed lines visible as a watermark in the sheet, which is more suited for writing papers, unless you particularly want to give a strong sense of direction in the texture of your image (figure 2.1). A 'wove' mould, with a structure like woven cloth, generally provides a more uniform paper texture which is preferable for pictorial purposes (figure 2.2).

Figure 2.1 'Laid' paper.

Figure 2.2 'Wove' paper.

2.2.3 Deckle edges

Handmade paper sheets have four 'deckle edges' which thin out irregularly where the pulp has seeped under the 'deckle' – the rectangular wooden frame used to retain the pulp in the mould. Cylinder mould made papers have only two deckle edges running the length of the roll, but may be cut into sheets in such a way as to produce 'false deckles'.

2.2.4 Wire and felt sides

The two sides of a sheet of fine paper usually differ discernably in a manner that reflects the method of manufacture: with a cylinder mould made paper, the so-called 'wire' side often shows a very fine geometrical diamond-mesh pattern, impressed by the wire screen on which the web was formed; the 'felt' side has a completely random fibrous texture, because it has only been in contact with the felt blanket of the machine. In the USA the 'wire' and 'felt' sides may be referred to as the 'screen' and 'nap' sides, respectively. Paper may be coated with sensitizer on either side, according to your taste for the image surface, and you can expect that the behaviour may differ both with regard to ease and volume of coating, and the appearance of the final print. The nature of the side may be detected by inspection under grazing illumination, or on close examination under bright transmitted light, what the papermaker calls the "look-through".

2.2.5 Watermarks

A watermark is caused by a local thinning of the sheet where a wire emblem has been woven into the mould, or into an additional roller in the cylinder machine. The reading of an unsymmetrical watermark, in different papers, cannot be relied upon to indicate which side is 'wire' and which 'felt'. Some manufacturers impress a watermark that reads correctly from the wire side, others do the reverse. The watermark itself must be excluded from the coated area, or it will become apparent in the finished print, but some workers prefer the watermark to be included in the margin as a token of authenticity. This is not always economically feasible; obviously papers with a frequently repeated watermark in the body of the sheet are not suitable.

2.2.6 Machine direction

An important characteristic of a machine-made paper, which is quite absent in hand-made papers, is the 'machine direction' – this is the direction in the sheet corresponding to the original direction of travel of the roll through the papermaking machine; the cellulose fibres naturally tend to partially align in favour of this direction. This slight directionality of the 'grain' has a consequent effect on the degree of expansion and the dimensional changes when the paper is wetted and dried. The relative change in length will be less along the fibre direction (i.e. the machine direction) than perpendicular to it (the cross direction). The paper is also more rigid along the fibre direction, so any natural curl of a sheet tends to occur in the cross direction. The paper also bends more readily in this direction, which provides a convenient test for determining which direction is which: cut two identically-sized strips of paper from the sheet, parallel to its edges, and at right angles to one another, marking their original orientation. Hold these together at one end horizontally; the paper strip cut perpendicular to the machine direction will bend more under gravity (figure 2.3) than the one cut parallel, which is stiffer. As a useful, but not infallible, guide, the machine direction often coincides with the longer dimension of a manufactured sheet.

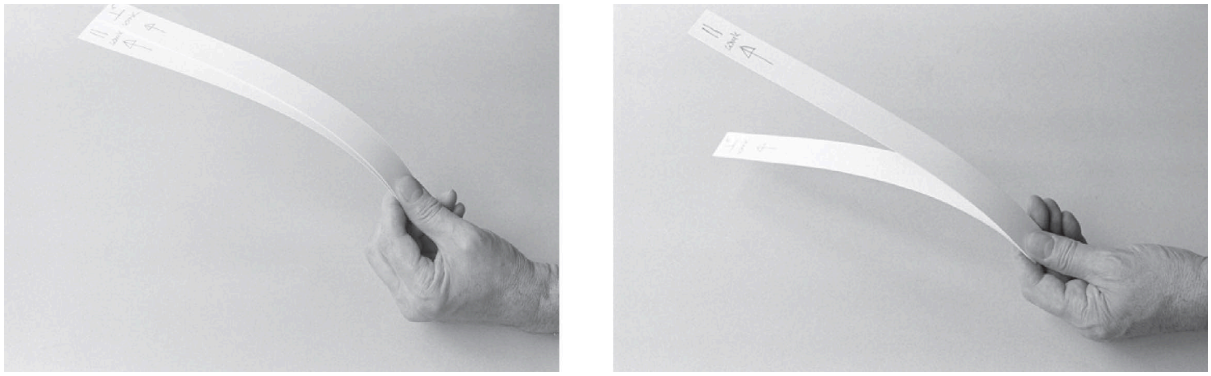


Figure 2.3. Demonstrating 'machine direction' in paper.

2.2.7 Surface texture

As a consequence of their treatment in manufacture, papers can have broadly three types of surface, called 'hot pressed' (HP), Cold pressed (CP) or 'Not' (meaning 'not hot pressed'), and 'Rough'. Hot pressed papers are usually calendered by passsage, under pressure, between heated rollers. The equivalent descriptions used by papermakers in other languages are:

English	**Hot Pressed**	**Cold Pressed**	**Rough**
French	Satine	Fin	Torchon
Italian	Satinata or Liscia	Fina	Grossa
German	Glatt		Rauh
Spanish	Liso	Fino	Gruesso

A fairly smooth, hot-pressed (HP) or cold-pressed (CP) surface is usually desirable for printing photographic images. 'Not' and 'Rough' surfaces may prove difficult to coat with sensitizer and may cause some loss of resolution in the contact printing. However, some heavily calendered, hot-

pressed commercial papers do not retain their smoothness on wet processing, which can cause them to swell and roughen perceptibly. Paper surfaces can be smoothed in the finished print by 'ferrotyping' against a metal plate, or pressing between perspex sheets in a letterpress.

2.2.8 Ream and sheet sizes

A 'ream' of paper may be defined as 480, 500, or 516 sheets, depending on its intended use, although the 500 sheet ream is becoming more common. The 'quire' is 1/20th of a ream: 24 or 25 sheets. The lack of standardization is not assisted by the fact that **t**here are more than 240 recognised sizes of paper sheet, each having a descriptive name which often derives from the nature of the emblem originally used as its watermark.[22] Only those sizes most commonly encountered in Europe as writing or drawing papers are listed here, and it should be appreciated that some papers intended for printing have the same name as those for writing, but a slightly different size. In the 'Double' sheet sizes, it is the shorter dimension of the parent sheet that is doubled; in 'Quad' sizes, both dimensions are doubled.

The International Standards Organization sizes for paper are now based on the 'A' series, beginning with A0, a sheet of area 1 m^2 with the lengths of its sides in the ratio 1: $\sqrt{2}$, i.e. 841 x 1189 mm (33.11 x 46.81 inches). All subsequent sheet sizes, A1 A2 A3 A4 etc., are obtained by halving the longer dimension of the previous one, consequently the ratio of the sides of the rectangle (its aspect ratio) remains 1 : $\sqrt{2}$ (1.414) throughout. Rather few fine papers are yet available in A sizes, however.

Table 2.1. Sizes of manufactured paper sheets for writing, drawing, and printing. The machine direction is usually the longer dimension.

Name of sheet	Size/inches	Size/mm
Pott	12.5 x 15	318 x 381
Foolscap	13.5 x 17	343 x 432
Post	14.25 x 19	362 x 483
Post (printing)	15.5 x 19.25	394 x 489
Crown ("Grande Couronne")	15 x 20	381 x 508
Large Post	16.5 x 21	419 x 533
Demy	15.5 x 20	394 x 508
Demy (printing)	17.5 x 22.5	445 x 572
Medium	17.5 x 22	445 x 559
Medium (printing)	18 x 23	457 x 584
Royal	19 x 24	483 x 610
Royal (printing)	20 x 25	508 x 635
Elephant	20 x 27	508 x 686
Double Crown	20 x 30	508 x 762
Imperial ("Jésus" in France)	22 x 30	559 x 762
Double Elephant	27 x 40	686 x 1016
Antiquarian	31 x 53	787 x 1346

When cutting up, or tearing large sheets into print-sized portions, it is worth planning the dissection to give maximum economy in the formats; the machine direction may also be a factor to consider, as is explained next. Many fine papers can be torn uniformly to give a sympathetic 'feathered' edge or 'false deckle', especially if they are folded first, then 'cut' with a blunt instrument like a paperknife. A steel ruler or large metal L-square, as used by builders, is useful to provide an edge against which large paper sheets may be torn, while checking the dimensions of the rectangle. (Some conservators consider it sacrilege to cut fine paper with knife or guillotine! Other workers claim that these instruments can leave behind tiny particles of metal that will mark the image.) Always take care to avoid touching the paper surface in the intended picture area: blotches in finished prints due to fingermarks can be very vexing, and wearing cotton gloves may be a useful precaution.

2.2.9 Dry and wet lengths

The length of any paper is greater when wet than dry, due to the expansion of cellulose fibres when moistened. However, in a machine-made paper, the sheet is dried under some tension, so its 'dry length' is still stretched; it will also have a 'stress-free dry length' which is shorter still, and which the paper reverts to when taken through a cycle of wetting and stress-free drying. These dimensional changes 'hydroexpansivity' (as a consequence of immersion in water) and 'hygroexpansivity' (due to changes in ambient RH) have some practical implications, especially for multiple printing.

In a machine-made paper sheet, these changes will differ in the two perpendicular directions, because the partly oriented cellulose fibres, when wetted, tend to expand more in width than in length. Changes in the cross direction are therefore greater than in the machine direction. When coating paper, it should be clipped or taped down along the machine direction, if possible, and coated in the cross direction, to allow freedom in the direction of greater expansivity. Likewise when mounting a finished print, the hinged mounts should be placed along the edge parallel to the machine direction, if possible, to minimise the buckling which may result from changes in ambient RH.

2.2.10 Paper Weight

The thickness of paper is specified by its 'weight', expressed per unit area. The usual units are grams per square meter, abbreviated as gsm or, preferably, g/m^2. For iron-based printing, a weight of ca. 160 to 240 g/m^2 is generally sufficient and convenient to ensure adequate wet strength for smaller (10 x 8 inch) prints; large formats (20 x 16 inch or more) may call for a heavier weight, ca. 300-360 g/m^2. Very heavy papers (ca. 500 g/m^2) will be slow to wash completely clear of residual chemicals. Thin tissue (20-30 g/m^2) can yield exquisite translucent prints – if you have the skill to coat and manipulate this fragile material; for this, a support of nylon mesh is needed at all times during the wet processing.

Some sources, especially in the USA, quote the weight of paper in the older measure of Imperial pounds (lbs) per ream; however this is meaningless unless the size of the sheet is also specified, and even the number of sheets per ream can vary in its definition. Application of a

conversion formula is possible, if these extra data are known, to give an equation to convert weights in lbs to g/m^2. The relationship between the weight, G, in g/m^2 and the weight, W, in lbs (pounds) per ream is:

$$G = WF/AS$$

Where:

A is the area of one sheet in square inches

S is the number of sheets per ream (which can be 480, 500, or 516)

F is a numerical factor converting the Imperial units to metric: the numbers of grams in a pound times the number of square inches in a square meter:

$$F = 453.6 \times 1550 = 703070$$

So, if we take a ream of S = 500 sheets of Imperial size (22 x 30 in.), the sheet area A = 660 square inches, and we get the conversion factor:

$$G = W \times 703070 / (660 \times 500) = 2.13\ W$$

i.e. a '90 lbs' Imperial paper is 2.13 x 90 = 192 g/m^2, etc.

2.3 Sizing Agents

A paper sheet that is completely unsized is called 'waterleaf', and is obviously highly absorbent – examples are blotting paper and filter paper. For printing paper it is essential to prevent complete penetration through the thickness of the sheet by an aqueous solution or ink; to retain liquid in the surface, papers for image-making of all kinds need to be rendered less permeable to water: this is achieved by the process of sizing, in which a substance is included in the paper sheet that inhibits its rapid penetration by water, either by partially blocking the capillary channels between the cellulose fibres or even by repelling the water. There are two essentially different methods of incorporating the sizing agent in the papermaking process:

2.3.1 'Tub' or 'surface' or 'external' sizing

in which the finished sheet is coated with a film-forming polymer as hydrophilic sizing agent, by brief immersion in a vat of a solution of the agent, and excess coating material is scraped off before drying, and possibly hardening. The usual agents are either some form of starch, or an animal gelatin, in which case a hardener, such as alum, is usually incorporated in the papermakers' sizing bath. The disadvantage of gelatin sizing to the manufacturer is that such sheets need to be dried in air or 'loft-dried', as it is known, for a considerable time, in order to 'cure' the size, and this demands a great deal of works space, and labour-intensive handling, and consequently expense. It is now reserved for the finest artists' papers. A method of surface sizing paper with gelatin for yourself is given below, but is rarely necessary today if a correct choice of paper is made.

2.3.2 'Engine' or 'body' or 'internal' sizing

in which a hydrophobic sizing agent is added to the pulp, or fibre suspension, *before* the sheet is formed. The traditional method is 'alum-

rosin' sizing: rosin is derived from the sap of coniferous trees and is mainly composed of abietic acid, a terpenoid substance which is water-repellant. When treated with sodium hydroxide this forms a water-soluble sodium salt which may be added to the pulp. This must then be treated with acid to re-form the resin size within the pores of the paper. The substance providing this acid is alum (potassium aluminium sulphate) which has an acidic reaction due to the hydrolysis of the hydrated aluminium(III) cation.[23] Such alum-rosin sized papers seem to work well with the siderotype processes, and were employed by William Willis for his Platinotype papers, but their archival stability has been questioned owing to the potential for acidity, associated with the alum.

Modern methods of internal sizing use reactive chemical agents called alkylketene dimers as additives to the pulp; the commercial substance has the trade name *Aquapel™* – or other equivalent – and is the 'neutral sizing agent' commonly employed by papermakers today. The molecule of this substance has a long saturated hydrocarbon chain, or 'tail' which repels water, and a 'head' consisting of a highly reactive functional group which can attach itself by bonding to the hydroxyl functions (–OH) of the cellulose molecule.[24] Thus water penetration is controlled by making the fibres somewhat hydrophobic. The advantage of internal sizing to the manufacturer is that no 'loft drying' is needed.

Papers may have both internal and surface sizing, but it is nonsensical to attempt to surface size a sheet with internal sizing agent. Papers that are additionally surface-sized with gelatin are particularly suitable for promoting the formation of red gold images, because gelatin acts as a 'protecting agent' for colloidal gold. But it is quite inimical to platinum printing, for reasons that I have explained elsewhere.

2.3.3 Surface-sizing paper with gelatin

Papers may be additionally sized with gelatin, if the effect this has on the print is considered desirable and necessary. Gelatin is available in a wide variety of forms and purities; gelatin may be derived from a number of species of animal skin, or bones; in the latter case it is referred to as an ossein. In the refining process it may have been cured either by acid or alkali (lime), and either oxidised or not. For gold printing, both types work, but there is a marginal preference for the acid-cured gelatin. The 'hardness' of a gelatin is measured by its Bloom number, which should be in the order of 180 or higher.

To prepare a 3% solution of gelatin for sizing, the solid gelatin must first be hydrated at room temperature by leaving it to swell in water. Weigh out ca. 30 g of gelatin and place in a large (>1 litre) beaker; add about 600 cm^3 of tapwater (filtered and dechlorinated). Leave the gelatin to swell at room temperature for ca. 30 minutes. Make up the solution to a total volume of 1 litre with water, and gently warm it on a hot plate, with stirring, until the temperature reaches 40–45°C (104–113°F); do not exceed this temperature otherwise the gelatin will be denatured. Stir gently, maintaining the temperature at 45°C, and all the gelatin particles will dissolve within half an hour. Transfer the gelatin solution to a dish maintained at about 40–45°C on a tray warmer. The paper sheets to be sized are now immersed in this for

about 10 minutes each, carefully brushing off any air bubbles on either surface. A stack of sheets may be interleaved in the bath. Drain, and remove excess gelatin by scraping with a glass rod or rubber squeegee, dragging each sheet across the edge of the dish, and dry each sheet at room temperature and humidity, by hanging it by one corner, changing the corner of suspension after an hour. The gelatin sizing solution may be re-used, but its storage life, even refrigerated, is limited to a few days and it will suffer decomposition unless preservatives are added.

Unhardened gelatin-sized papers have a slimy surface texture and the gelatin tends to pass into the wet-processing baths, so a hardener is needed, to cross-link the gelatin molecules rendering it harder and more insoluble, before the paper is coated with sensitizer. The usual hardening bath has for many years been a solution of formaldehyde, of strength about 1 to 2%.[25] However, formaldehyde is a noxious and unpleasant substance to handle, especially in a confined space, so a few years ago the author suggested the use of another hardening agent to the alternative process community, which is much less offensive due to its lower volatility: glyoxal; this seems to have been widely and successfully taken up by current practitioners.[26] Papers should be hardened in a 2% glyoxal bath for about 10 minutes at room temperature, followed by a water wash of 20 minutes to remove excess hardening agent, which may otherwise cause fogging of the sensitizer.

An alternative procedure, which has the merit of economy, is to size the paper sheets by brushing the solution onto one side only. Only about 1/10th of the volume of sizing solution need be made up (3 g of gelatin in 100 cm^3 of water) and the hardening agent may be added to this solution directly (5 cm^3 of 40% glyoxal) for a batch of 10-20 sheets of 10 x 8" paper.) A wide 'Hake' brush should be used to perform the coating.

When internally-sized papers are subsequently coated with a film of hardened gelatin, blisters can arise in the wet processing procedure, because water diffuses through the semi-permeable membrane formed by the gelatin and can remain trapped on the surface of the sheet. If a correct choice of manufactured paper is made in the first place, it is unlikely that additional surface sizing will confer any benefits.

2.3.4 Surface-sizing with starch

In papermill practice, surface sizing with starch does not employ the usual familiar substance of that name, but rather a derivative called "oxidised starch": this product of treating starch with either hydrogen peroxide or sodium hypochlorite as oxidants, has reactive functional groups, especially carboxylates, which can bind the iron(III) (as indeed they do in ferrioxalates and ferricitrates) and thus diminish the efficiency of the sensitizer, shortening the exposure scale, and possibly sequestering iron(III), which eventually causes staining. In general, no good purpose is served by starch-sizing a paper intended for siderotype processes.

2.4 pH Buffers

To conform to International Standards, papers intended for archival or fine art use are now required to be buffered to an alkaline pH, usually with added

chalk (calcium carbonate), to protect them from the damaging long-term effects of acid, and they are commonly so advertised. But it is now widely acknowledged among alternative photography practitioners that papers intended for siderotype should contain no chalk, which is hostile to the iron(III) chemistry, its alkalinity causing hydrolysis of the Fe(III) complex and precipitating insoluble calcium oxalate, (the same substance that causes some types of gall stone). Pretreatment of a chalk-buffered paper with dilute acid (1-2% hydrochloric acid or 5-10% sulphamic acid) will remove the chalk. The popular use of oxalic acid for this purpose is obviously chemically inappropriate. The quoted pH of the paper should be 7 or less, i.e. on the acidic side, so as not to promote hydrolysis of the applied iron sensitizer.

This requirement is contrary to the thinking on paper conservation, which favours the incorporation of buffers to prevent acidic embrittlement. However, with the present use it does not matter, from the conservation viewpoint, if the paper is fairly acidic initially, because in the course of wet processing it will be passed through baths that effectively de-acidify it and bring it to a favourable pH of 9 or so, before the print is finally dried.

2.5 Other Additives

Papermakers may chose to include a variety of other chemical additives in their products – doubtless for the best of reasons, in view of the use for which their paper is intended. In this regard, it should be remembered that they very seldom have the alternative photographic process printer in mind. Not all of the following additives are necessarily deleterious, but if problems arise, these are the first things to avoid:

- **Retention aids**. These are added to the pulp at the wet end of the mill, in order to improve the trapping by the wire screen of fine particles of fibre, fillers, and other additives. Excessive use of retention aids is known to exacerbate flocculation, and they are likely to cause image "blotching" for the following chemical reasons. Retention aids are organic polyelectrolytes of very high molecular weight, such as cationic polyacrylamides (CPAM), or cationic starch; they consist of long polymer chains bearing many positively-charged groups (quaternary alkylammonium cations) that will exert a strong attraction on the small, mobile, negatively-charged anions present in ammonium ferric oxalate photosensitizer chemistry. These anions are liable to be trapped by local concentrations of the huge cationic polymer and rendered less reactive, thus wreaking havoc with the sensitive printing-out photochemistry.
- **Optical Brightening Agents** (OBA) – fluorescent substances that make the paper appear extra-white, sometimes unnaturally so. Their archival stability has been questioned.
- **Fillers** such as clay, to give the paper and smooth and shiny look.
- **Wet strength agents** which inhibit disintegration of the wetted paper.
- **Bleaches** used to decolorise delignified woodpulp – the so-called 'woodfree' papers.
- **Dyes or pigments** to stain the background for various purposes.

2.6 Choice of Paper for Siderotypes

To summarise: the best results with ferric processes will be achieved on a high-quality fine-art paper, hand- or cylinder-mould made, having the following characteristics:

- A pure cellulose furnish, preferably long fibres as for security papers.
- A 'wove' mould; any watermark excludable from the picture area.
- A smooth, hot-pressed (HP) or cold-pressed (CP) surface.
- Internal sizing with Aquapel™ or equivalent alkyl ketene dimer (AKD)
- Gelatin-sized only for the special case of 'red' gold.
- No alkaline buffering agents such as chalk (calcium carbonate).
- No retention aids such as CPAM or other additives whatsoever.
- A weight of ca. 160 g/m^2 (small sheets) to 360 g/m^2 (large sheets).

The greatest imponderable in 'plain paper' printing is the effect on the reactive sensitizer chemicals of the paper-makers' additives, which they are usually reluctant to disclose or discuss. Each commercial paper has its own idiosyncrasies, which may even vary from batch to batch or be changed by the manufacturer without notice. There is no substitute for personal trial and experiment. Once you have discovered a satisfactory paper, it is wise to invest in a substantial amount of the same making.

Several mould-made fine-art papers intended for watercolorists or printmakers that have been found to work well with the chrysotype process are listed in Table 2.2, they are all available with a HP or Not surface.

Table 2.2. Cylinder mould-made papers generally suited for siderotypes

Name	Furnish	Sizing	Comments
Arches Platine	100% cotton	aquapel	unbuffered
Arches Aquarelle	100% cotton	gelatin	neutral pH
Atlantis Silversafe Photostore	100% cotton	aquapel	pH 6, unbuffered
Bergger COT320	100% cotton	gelatin	unbuffered
Fabriano 5	50% cotton	hard gelatin	acid free
Hahnemühle Platinum Rag	100% cotton	specialty	unbuffered
Herschel handmade	100% flax	aquapel	unbuffered
Hollingsworth Kent Drawing	100% cotton	internal	acid free
Legion Revere Platinum	100% cotton	specialty	unbuffered
Saunder's Waterford	100% cotton	gelatin	pH 8.5 buffered
Strathmore 500	100% cotton		ultra-smooth
Wyndstone Vellum	wood cellulose		lignin free

Since they do not fulfill all the criteria listed above, there is no guarantee that any given paper will always "work" with every process.

2.7 Storage and Handling of Paper

Paper should be stored at an appropriate RH: no greater than 65% RH, above which the growth of mould may occur,[27] and preferably not at too low an RH either, otherwise the dry sheet may imbibe an excessive amount of sensitizer when coated. Storage at very low RH may be compensated by humidifying

the sheet for 20–30 minutes over a bath of water at room temperature just before coating.

Paper sheets should always be handled only by the margins, using both hands to avoid creasing large sheets. Never touch the picture area, either before or after coating, and do not touch the reverse either, because moisture and oils from the fingers can rapidly diffuse through the sheet. Cotton gloves are useful to protect paper from fingermarks.

2.8 Sensitizer Absorption and Wetting Agents

The density of paper is ca. 0.75 g/cm^3, whereas that of crystalline cellulose is ca. 1.5 g/cm^3: this tells us immediately that paper is about 50% empty space – a void which can be partly filled by imbibing liquids. There are essentially two interconnected systems of pores within the structure of cellulose paper:

1. The *macroporous* structure, which consists of the capillary channels between the cellulose fibres, easily visible with a hand lens. This provides a route for the imbibed fluid into the interior, but this volume is not useful for retaining nanoparticle image substances, because their particles will easily be washed out of these regions.
2. The *microporous* structure within the cellulose fibres; which is provided by gaps between the fibrils that make them up. This region, known as the interfibrillar space, can effectively trap the nanoparticles of image substance which are formed within the fibrils. Penetration of the interfibrillar space of the cellulose structure by the sensitizer solution is therefore of paramount importance, if the image is not to wash away in the wet processing.

In practice, not all of this space is accessible, and cellulose is usually found to absorb ca. 40% of its own weight of water, thus a volume of 1 cm^3 of 'waterleaf' paper, weighing 0.75 g, will absorb a maximum of 0.3 g (= 0.3 cm^3) of water = 30% by volume. The volume of sensitizer applied in coating is related to the depth to which the solution penetrates the paper. Experimentally, the coating of a well-sized paper, by the less wasteful rod method, is found to use ca. 1.5 cm^3 of sensitizer to cover the area of an A4 sheet, which is 1/16th of a square meter. The specific coating volume, per unit area of surface, is therefore in the order of 16 x 1.5 = 24 cm^3/m^2. This would correspond to a 'layer' of liquid of thickness 24 µm (ca. 1 thousandth of an inch). But saturation of the cellulose structure only occupies ca. 30% of its volume, so the thickness of the layer of paper that is penetrated by sensitizer is about 24/0.3 = 80 µm or 0.08 mm. This calculated thickness of the sensitized layer appears to agree broadly with measurements made on actual coatings under a microscope.

The degree of internal sizing with Aquapel™ should be high enough to make the sheet somewhat hydrophobic initially, *i.e.* slightly water repellant. This is intended to allow time for an aqueous sensitizer to be uniformly spread over the surface of the sheet before it starts absorbing into the fibres. It is undesirable that a sensitizer should soak rapidly into the interior of a paper sheet, where it cannot contribute to the image and may resist washing out, besides being very wasteful of the sensitizer chemicals.

Workers with the iron-based processes must recognise that the absorbency of a paper also depends on the nature of the solution being

applied to it. Important factors are: the viscosity, surface tension and chemical composition, which influences its ability to swell cellulose and open micropores in the cell wall, so admitting further liquid into the interfibrillar space. For instance, sensitizers employing ammonium iron(III) citrate (*Argyrotype, Vandyke*, *Brownprint*, and traditional *Cyanotype*), which has a large molecular structure, cannot easily penetrate the interfibrillar space; the sensitizers just tend to lie on the surface of the paper or in the open macroporous capillaries, rather than diffusing through the pores into the interfibrillar space. Two problems may result: first, when the coating dries, crystals may be formed on the surface, which will leave marks on the image and may damage the photographic negative on contact printing; and second, much of the image substance will tend to wash out during the wet processing, because its nanoparticles (often of nanometre dimensions) are not physically trapped within the interfibrillar capillaries; the result will be a weak and disappointing picture.

To help overcome these problems, and to control the absorption of sensitizer, a wetting agent, or surfactant, may be added. There are three broad categories of surfactant, depending on their molecular structure: cationic, anionic and non-ionic. The ionic agents have a tendency to react with the ionic species in the sensitizers and may cause precipitation, so I favour non-ionic surfactants, such as Tween 20™,[28] at a final concentration of about 0.2-0.5%, depending on the paper, which seems compatible with all the usual sensitizer chemicals. This is inexpensive and readily obtainable, though no doubt there may be many others that are also suitable; however the longer chain congeners such as Tween 80™ etc., should be avoided beause they tend to cause foam.

In contrast to the problem presented by ammonium iron(III) citrate, sensitizer solutions based on ammonium iron(III) oxalate (printing-out *Platinum, Palladium, New Chrysotype* and my *New Cyanotype*) appear to penetrate cellulose fibres quite readily: they suffer less from the problem of 'washout' or 'bleeding', and require very little additional wetting agent (0.2% at most, helps to reduce the contact angle and facilitates coating). Too much surfactant will allow the sensitizer to diffuse too deeply within the paper, the image will appear 'flat' and 'sunken'. The control of the balance of paper absorbency towards the sensitizer solution is crucial to the image quality, and is the main key to success in hand-coated photographic print-making.

2.9 Methods of Coating Paper

In place of the traditional brush, or foam-rubber applicator, the more economic coating instrument that has gained wide acceptance among alternative printers, since the author and Pradip Malde introduced it in 1986, is the glass coating-rod. However, it is said "there is nothing new under the sun", and we have since discovered three historical references, from 1853, 1856, and 1861 to the use of glass rods for coating, suggesting that it was standard practice at the time (figure 2.4)![29]

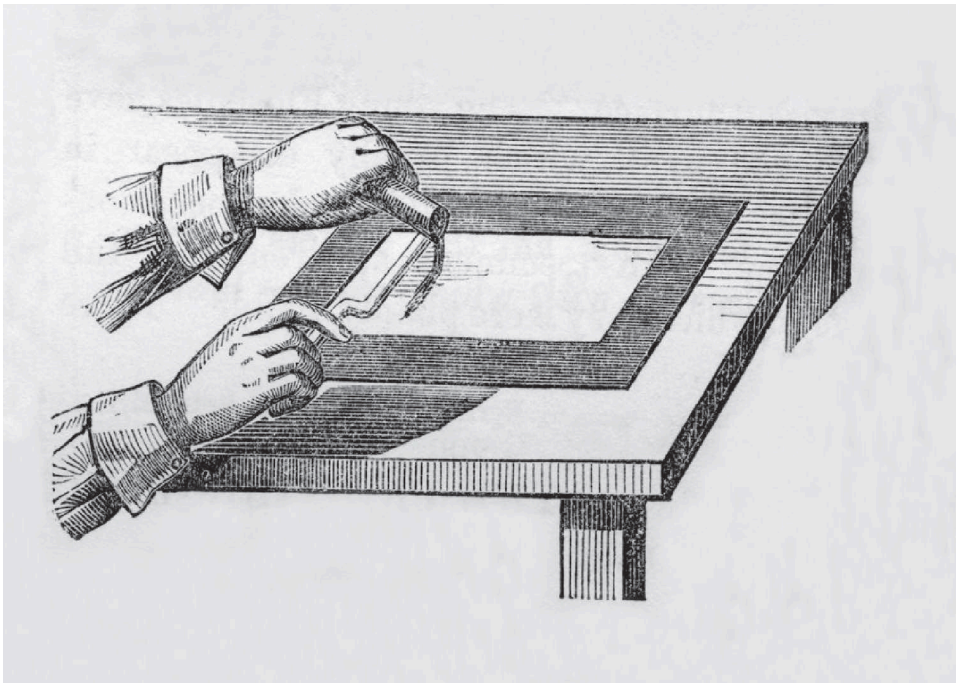


Figure 2.4. Etching from 1850 showing a glass rod used to coat paper.

The implement that we recommend today is preferably a thick-walled glass capillary tube, rather than solid rod, because the tube is usually manufactured to higher standards of straightness than the rod; this may be checked for 'ripples' by looking closely along its length, held to the eye against the light. An external diameter between 9 and 12 mm is suitable, with a wall thickness of at least 3 mm. The end portions of the rod should be bent at an obtuse angle, using a powerful gas torch; a bicycle handlebar shape: _____/ is simple and ergonomically effective in use, although more exotic shapes may be tried if you are a capable glass worker (figure 2.5).

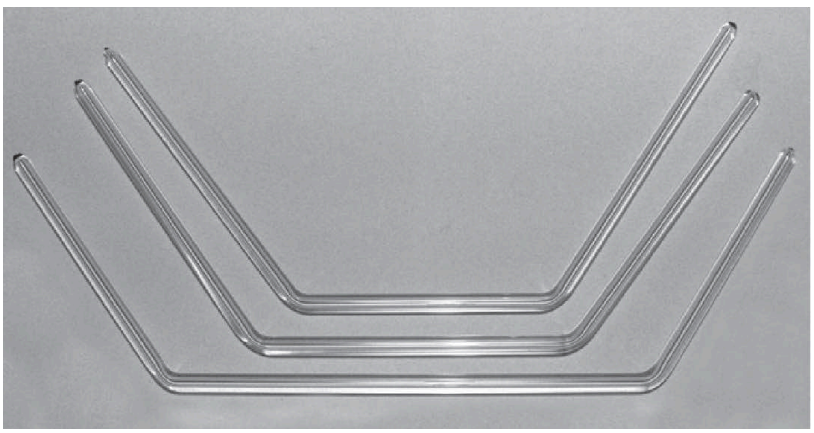


Figure 2.5. Simple coating rods of glass tubing.

The straight central section of the rod acts as the spreader, and the distance between the bends determines the width of the area coated; the limbs serve as handles. This implement must be kept scrupulously clean and free of grease film. An appropriately-sized rod will be needed for each format to be printed. It is usual to make it equal to the shorter dimension of

a rectangular frame, and this is particularly recommended in the case of panoramic formats.

A commercial version of this device has been marketed in the USA; called the 'Puddle Pusher™', it is obtainable from suppliers in North America, and has a central flat handle cemented onto an open-ended glass tube. Unlike the version described above, it is designed for use one-handed, and care is needed to ensure that sensitizer is not deposited inside the open tube.

2.9.1 Coating by glass rod

Follow this procedure, observing all the advice:

1. Cut or tear your sheet of paper to an appropriate size that allows generous borders around the picture area (but still fits into your printing frame, of course) – this not only looks well, but the margins also facilitate handling and protect the image. The wider the borders, the less likely is the sheet to curl or cockle when its central area is wetted with sensitizer and the fibres expand.

2. Having identified the wire and the felt sides of the paper, as described above, decide which you wish to coat, and mark the sheet very lightly in soft (2B) pencil to locate the corners of the area to be coated. Time and trouble may be saved by devising a card template to guide this marking-up for standard formats. Alternatively, the paper sheet can be placed on a light-box which has four small pieces of dark tape appropriately disposed to indicate the marking postions – the light box also has the advantage of revealing any flaws in the paper, and checking whether the side is "wire" or "felt". The dimensions of the coated area should be ca. 1 to 2 cm larger than the negative to allow for irregularities and to make it easy for you to position the negative correctly in the printing frame. Avoid including any watermark within the picture area.

3. Tape or clip the sheet lightly to a perfectly flat, level surface: a heavy sheet of plate-glass is ideal. The heavier weights of paper (>200 g/m^2) need only be held at the top of the sheet, but thin papers and those prone to curling should be held down at the bottom also, otherwise it may ruck up during the coating operation. Use low-tack drafting tape not masking tape. It is preferable if you can arrrange that the machine direction in the paper runs away from you, perpendicular to the coating rod, rather than from left to right.

4. Check with a spirit level that the paper is horizontal, left to right; this is critical for successful coating, so adjust it if necessary by 'shimming up' the baseplate with strips of thin card. It is not so important that the paper should be level in the back to front direction.

5. Dust off the paper surface with an air-blower, and ensure there are no hairs or particles in the coating area.

6. Choose a syringe of appropriate size and ensure its plunger is fully depressed, then, keeping the nozzle below the liquid surface, draw up the mixed sensitizer into the syringe, some way above the volume required. Carefully expel excess sensitizer back into the vessel to adjust it to the required volume: ignore the small air bubble in the syringe and take the volume reading from the *bottom* of the plunger. A 10”x8” print will require between 1.4 and 1.6 cc, depending on the paper, and other sizes in proportion to their area. Try to ‘fine tune’ this volume with your experience of a particular paper, so as to avoid excess sensitizer which is wasteful and may cause problems by crystallization.

7. Place the tip of the syringe on the bottom left pencil mark and expel the liquid slowly and gently from the syringe (use two hands) as you traverse it steadily from one side to the other across the width of the coating area between the pencil marks at the bottom of the paper; reverse direction and go back again if all the liquid is not expelled. For steadiness, touch the paper lightly with the syringe nozzle and try to form an unbroken strip of sensitizer, but do not be too slow or fussy – irregularities will even out in the coating. (Occasionally the syringe plunger may judder and send a jet of solution across the paper – do not panic! Continue swiftly and the coating should rectify this. This occasional experience is why we coat from the bottom up, rather than the top down.)

8. Take up the spreading rod with an end in each hand, place the straight central portion onto the paper parallel to, and a little below, the strip of sensitizer. Then, with slight pressure, push the spreading rod up into the strip of solution. Pause briefly at the pencil marks (a couple of seconds) while the liquid distributes itself uniformly along the length of the rod, then steadily push the strip of solution up the paper, like a tiny tidal wave running in front of the rod. The rod is not rotated, and very little pressure need be applied. When you reach the pencil marks at the top of the coated area, very gently lift the rod, keeping it parallel to the paper surface, and ‘hop’ it over the strip of solution and pull it back down to the bottom of the coating; then hop over the sensitizer strip once more and push it up to the top to repeat the spreading. Just six passes over the paper should suffice for its surface layer to become saturated with a uniform coating of sensitizer. Make the first two passes quite rapidly (3 or 4 seconds each) to ensure complete wetting of the surface, and the last four as slowly as possible (10 to 15 seconds each) to allow maximum absorption. At the end of the sixth pass, drag the spreader below the picture area, with its excess sensitizer (which should be very little when you have fine-tuned the exact volume to use with your chosen paper.

9. Lift off the spreader very gently (otherwise unwanted drops may splash onto the paper), and soak up any residual liquid left at the bottom of the coating with the edge of a clean strip of blotting paper laid up to the pencil marks. If this is not done, crystals may be formed which can damage the negative. Rinse the spreading rod immediately under the tap, unless you are coating several sheets at one time.

Occasionally a paper may be encountered that is difficult to coat by this method, because the strip of sensitizer solution contracts into 'beads' as it is pushed up the paper and blank streaks are left behind in the coating. This problem may be rectified by applying two strips of the sensitizer solution, one at the bottom and one at the top of the coating area; if the continuity of the coat 'drops out' on the first pass, the fresh strip of sensitizer picked up from the top with the rod will put this right. It may also be helpful to place a thin sheet of sponge rubber or plastic foam (Plastazote) between the paper and the glass plate, to take up any variation in thickness (which is common in handmade paper) or unevenness in the glass rod. Additional wetting agent (Tween 20 - see below) may also assist the evenness of the coating by reducing the surface tension of the solution and thereby reducing the contact angle between sensitizer solution and paper.

I suggest that, before attempting this technique with precious metal solutions, you should hone your skill at it by practising with an aqueous solution of vegetable dye, which will show the evenness of your coating.

2.9.2 Coating by brush

The traditional method, for those who prefer a more 'painterly' style of coating, or who wish to apply the sensitizer more selectively, is to use a brush. This can be hard to keep clean, and tends to be very wasteful, consuming at least twice as much sensitizer as rod coating, which is a serious disadvantage when the sensitizer solution like chrysotype costs about £0.20 per drop. Brushes with metal ferrules must be avoided because the sensitizer chemicals will react with the metal, to the detriment of both. A broad Japanese Hake brush, of the type available from most art shops, is quite suitable.

The sensitizer is poured along the paper, just outside one edge of the picture area, and spread by means of a brush, previously dampened with distilled water, making long even strokes in a consistent direction to cover the area, then repeating the brushing at right angles. If sufficient sensitizer remains, the brushing may be continued until it is all absorbed. Foam-rubber applicators have been advocated as a substitute for brushes, but these too are very wasteful in holding back a substantial amount of sensitizer which never reaches the paper.

2.10 Drying Sensitized Paper

Immediately after coating, the paper should be left horizontal for a few minutes until the liquid is sufficiently absorbed into the fibres for the reflective sheen of the surface to disappear. If the sheet is prematurely heat-dried, the sensitizer will simply form a layer on the surface, and the image substance will wash off in the wet processing instead of being trapped by the paper fibres. The sheet may then be hung up, or left on a drying screen, or placed in an empty drawer or cupboard, to dry in the dark for an hour or more before use. It helps if the air can be gently circulated evenly over the surface of the paper by a fan or blower; optionally some heat may be used - a stream of warm air at 40°C for 10 minutes is adequate. Such a flow should be well diffused by a plenum or baffle within a box, to achieve uniformity, which is very important. The prevailing relative humidity profoundly affects

colour, so heating directly, e.g. with a hairdrier, can cause hot-spots which tend to produce uneven results and conspicuous irregularities, food driers can also develop 'hot spots'. Heat-drying sometimes causes a 'graining' of the texture, when the paper fibres become conspicuous.

2.11 Enclosures for Regulating Humidity

The amount of water present in the fibres of the sensitized paper at the time of printing is a crucial factor in determining the characteristics of the final print, as is explained in Appendix IV. It affects the extent of print-out, the colour, and the contrast. If you want reproducible results in your prints, and your working environment has an unsuitable or somewhat variable RH, as many do, you will have to take the trouble to regulate paper humidity. *There is no alternative to careful control of this parameter*. Fortunately this is not difficult, and can be accomplished with a simple piece of inexpensive equipment. It is totally unnecessary to install humidifiers or air-conditioners for controlling the RH of the entire volume of your workspace - and the RH that you require for your gold print may be quite different, anyway, from that needed for your personal comfort. By using controlled RH enclosures, you can exercise a major control over the appearance of the gold image that will actually cost you nothing - except a little time - to apply. I emphasise this point because it has been asserted by some dealers in alternative process materials, that the business of controlling humidity in a paper sheet is far too troublesome and 'user-unfriendly' to merit consideration by their customers. In this they are misled by their lack of understanding of the factors important to the process. The principle is no different from the use of a traditional humidor for conditioning cigars before smoking, and is effective for a similar reason: the tobacco leaf, after all, is mainly constituted of cellulose. If smokers are prepared to go to this degree of trouble to perfect their pleasures, why shouldn't you? Similar considerations in the past determined the suitable geographical locations for the British cotton-spinning and weaving industry, because of the favourable effect of a stable, high ambient RH on the pliability of cotton fibres.

There are two different methods for regulating the humidity in a sheet of coated paper, which I shall call, for good scientific reasons, the *Equilibrium Method* and the *Timed Method.* Each has advantages, and disadvantages, which you can assess and make your own choices.

2.11.1 Equilibrium method

The principle that the relative humidity of the ambient atmosphere influences the concentration of water in the paper fibres is explained in Appendix IV with reference to the cellulose adsorption isotherm. The RH is fixed within a controlled humidity chamber, which contains a saturated solution of a salt in continuous contact with excess solid, at a specified temperature, usually 20°C. The RH values of many such solutions have been determined, but the salts listed in Table 2.3 will be found most convenient. Many more salts, and mixtures, have been used to obtain intermediate RH values, see the literature for extensive lists.[30] The chemicals listed in Table 2.3 above have been selected for their convenience, relative cheapness, and low toxicity. For practical purposes, and in the interests of economy, you can

start with only three controlled humidity chambers containing, respectively, solid anhydrous calcium chloride (RH 9%), saturated calcium chloride (RH 32%) – which is conveniently made from the solid when it becomes too tacky – and either ammonium chloride (RH 80%) or common salt (RH 75%).

Table 2.3. Substances for making constant RH enclosures (at 20°C).

No.	Substance	Formula	RH%	Solubility g/litre
H1	Calcium chloride anhydrous	$CaCl_2$	9	use solid
H2	Lithium chloride	LiCl	15	800
H3	Calcium chloride	$CaCl_2$	32	750
H4	Potassium acetate	CH_3COOK	35	2560
H5	Potassium carbonate	K_2CO_3	44	1100
H6	Calcium nitrate	$Ca(NO_3)_2$	56	1290
H7	Sodium chloride	NaCl	75	360
H8	Ammonium chloride	NH_4Cl	80	372

The RH in such a system varies very little with temperature provided a saturated solution is maintained by contact with excess solid (The natural tendency for the vapour pressure of water to increase with temperature tends to be offset by an increase in the solubility of the salt, in most cases). However the absolute humidity, measured as the weight of water per unit volume of air, does increase with temperature, (see Table in Appendix IV.1).

2.11.2 Timed method

The alternative method of regulating humidity, or degree of hydration of the paper, is simpler and cheaper, but less reliable. It requires you to make a *timed* exposure of the coated paper to an atmosphere having RH of 100%. i.e. using a chamber containing only pure water, at room temperature.

Unlike the equilibrium salt solution chambers, where the paper can be left for hours, this exposure to 100% RH must be timed for reproducibility, and it should not be excessively lengthy, up to a maximum of 30–40 minutes, or the paper will imbibe far too much water, with consequent degradation of the image quality. If left in such a 100% RH bath, cellulose goes on absorbing water into its capillaries until it is perceptibly 'soggy' and useless for image-making, and damaging to negatives. The effects of low RH are achieved by exposing the sheet for only a minute or two, but it can introduce problems of non-uniformity. It is important to keep the humidifying chamber at a uniform and constant temperature, about 18–20°C, because the vapour pressure of water increases steeply with rising temperature.

2.11.3 Effect of humidity on printout

The result of using a high degree of hydration of the sensitized paper is a printing-out processs, in which a complete, or nearly complete, image is formed by the light during the exposure, and requires little or no subsequent development. Such a process has three advantages over the development process that occurs at low degrees of hydration:

- the ability to inspect the image, at any stage of the exposure, by means of a hinged-back printing frame, does away with the need for prior test-strips;
- there is a self-masking effect in print areas of high optical density, which proportionally resist further darkening; negatives of long density range are accommodated simply by extending the exposure to 'bring down' the highlights without 'blocking up' the shadows;
- there is no need for a developer.

The present methods have been evolved with a view to optimising the printing-out effect; in particular, the composition of the sensitizer and the control of humidity are important.

2.11.4 Construction of hydration enclosures

You will need a fairly shallow opaque (preferably red) plastic box larger than the paper size, provided with a flat rigid lid, also opaque, offering a reasonably air-tight seal. A sheet of glass covered with black paper can also be used as a lid. Cat litter trays are ideal for this purpose; photographic dishes are too shallow and have a lip which makes sealing difficult. To maintain very low RH it is best to fit a strip of sponge draught seal around the rim of the tray and use clips to secure the lid to it under slight pressure.

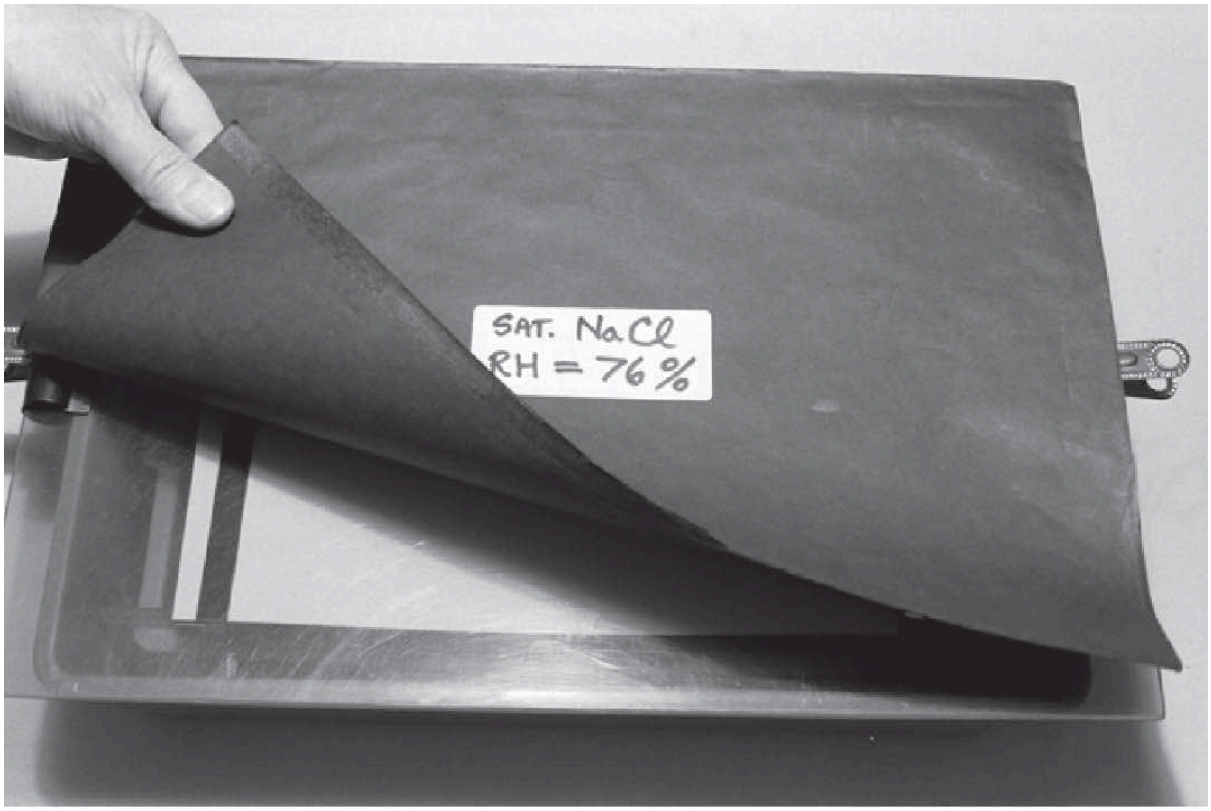


Figure 2.6. Box for hydration of paper.

The sheet is supported, coated side down, on a cross-hatch of plastic rods, larger than the coated area but smaller than the paper, which are positioned well above the liquid surface. If the solution is contained in a smaller tray or dish, nested inside the main enclosure, you will find it much

more convenient to change or renew, and furthermore it will be better protected against temperature changes due to draughts.

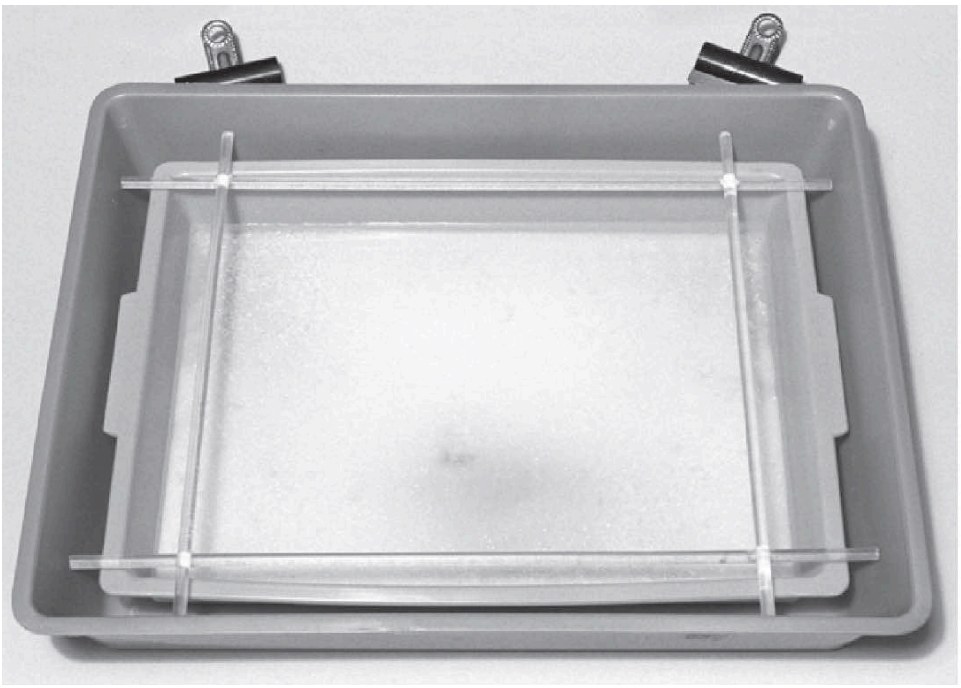


Figure 2.7. Paper support in hydration box.

If you are making small prints or test pieces, a plastic sink mat supported at suitable height above the surface of the liquid is convenient to support the sheet face up. It is essential that during hydration the sensitizer coating does not touch anything at all.

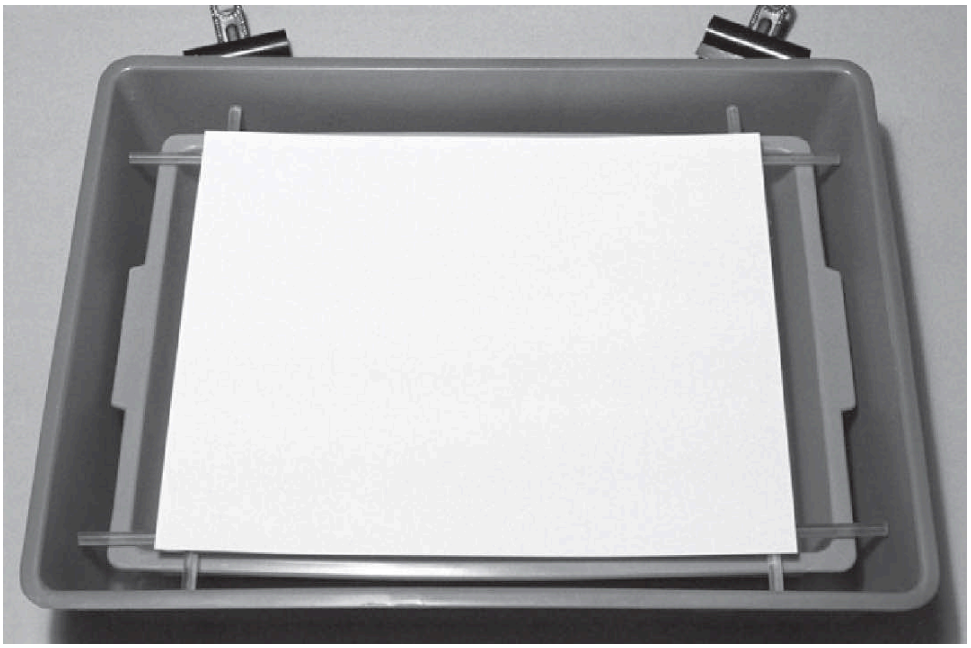


Figure 2.8. Paper sheet in position for hydration.

Alternatively, the sheet of sensitized paper can be held securely on the underside of the lid, coated side facing down, by two strips of self-adhesive

magnetic tape, which is quick, clean, easy to use, and does not mark the paper.

For efficiently humidifying the print *after* exposure, but before the wet processing baths, hydration chambers containing only water may be operated above room temperature, typically on a photographic dish warmer held at a temperature of around 40°C. There will be considerable reflux of water at this temperature, so it is best to use two lids, keeping one dry to avoid excess condensation finding its way onto the print.

2.12 Suppliers of Fine Papers

UK

John Purcell Paper
15 Rumsey Road
London
SW9 0TR
UK

Tel: +44 (0)20 7737 5199
Fax: +44 (0)20 7737 6765
Email: mail@johnpurcell.net
https://www.johnpurcell.net

Hahnemühle UK Ltd.
Suite 5, St. Mary's Court
Carleton Forehoe
Norwich
NR9 4AL
UK

Tel: +44 (0)1603 759266
Email: uksales@hahnemuehle.com
https://hahnemuehle.co.uk/
https://www.hahnemuehle.com/en/index.html

Jackson's Art Supplies
1 Farleigh Place (off Farleigh Rd)
Stoke Newington
London
N16 7SX
UK

Tel: +44 020 7254 0077
https://www.jacksonsart.com/jackson-s-paper-guide

Continental Europe

Arches
48 route de Remiremont
88380 Arches
France

Tel: +33 3 29 32 60 00
Fax: +33 3 29 32 74 96
Email:
https://arches-papers.com

Ruscombe Paper Mill
23 Cours de La Marne
F-33460
Margaux
FRANCE

Tel: +33 557 887 377
Email: info@ruscombepaper.com
http://www.ruscombepaper.com/

Bergger

Tel: +33 9 66 89 50 26
https://bergger.com

USA

Legion Paper

Tel: 212 683 6990
Email: info@legionpaper.com
https://legionpaper.com

Jerry's Artarama
6104 Maddry Oaks Ct
Raleigh
NC 27616-9997
USA

Tel: 800 827 8478
https://www.jerrysartarama.com

Reich Paper
7518 Third Avenue
Brooklyn
NY 11209
USA

Tel: 718 748 6000
Fax: 718 238 5400
https://reichpaper.com

3. Chemical Practice

3.1 Warning and Disclaimer

Most of the chemicals used in the processes described in these pages are hazardous in some degree, and, although none are seriously toxic, all of them should be treated as potentially harmful. It is the responsibility of anyone who choses to work, or who causes others to work with hazardous materials, to inform themselves in advance about the dangers, and to ensure that they take precautions to safeguard themselves, other people, and the environment. Full information regarding hazards may be obtained from the Materials Safety Data Sheets, (MSDS) which are available from suppliers of chemicals or by consulting any reference manual on chemical safety. They may also be consulted on-line: lists of web sites carrying the MSDS may be found at:

http://www.ilpi.com/msds/index.html
http://www.msdssearch.com/DBLinksN.htm
http://www.msdsonline.com

A summary of the relevant hazards will be found in Appendix I.

The author and publishers of this book hereby deny liability for any consequent injury, sickness, damage, or loss resulting from the use of the information contained herein.

3.2 General Advice on Chemical Manipulations

Non-chemists rarely appreciate that the order in which reagents (i.e. reactive chemicals) are mixed may affect the outcome: in many chemical reactions, it does matter whether we add A to B, or B to A, owing to the effects of having one reagent or the other initially present in excess. For instance, it can make the difference between forming a precipitate (i.e. an insoluble solid thrown out of solution) or not - which in turn may leave behind some tiny particles which can cause imperfections in the print. If there are more than two reagents to be mixed, it is vitally important to mix them in the correct order specified. The following remarks apply to all chrysotype sensitizers.

3.2.1 Practical safety considerations

Before commencing any practical work, it is entirely your responsibility to take the trouble to acquaint yourself with the hazards presented by the chemicals that you are going to use: these are summarised in Appendix I. When working with chemicals, you should always take the minimum precautions of wearing eye protection (or, at least, conventional prescription spectacles) and a laboratory coat, smock, or plastic apron as an easily-discarded protection against spills or splashes. Gloves are not essential protection for manipulating the chemicals used in this work (except in Appendix II), unless you happen to be particularly susceptible to skin allergies: the insensitivity of touch caused by gloves can sometimes represent a greater risk than bare fingers. In the event that any of these chemicals should come into contact with your skin, wash them off

immediately with plenty of cold water, and it is most unlikely that you will suffer any harm.[31]

It is important to label your made-up chemical solutions fully, and it is wise to keep a record of how and when they were made up in a laboratory notebook. The security of your chemical stocks is an obvious responsibility, especially if there are children on the premises.

3.2.2 Cleaning glassware

Strong detergent, bottle brushes, and hot water should be used to remove films of grease from glassware and storage bottles. Particularly resistant deposits of solid may need a scouring powder. The criterion for a clean glass surface is that water can be seen to wet it and drain off in a uniform film – without beading into droplets. Most chemicals used in this work are highly water-soluble, so glass apparatus should only need thorough rinsing to clean it, if it is grease-free. Be sure to rinse sufficiently; think of this process as successive dilutions of a contaminant by a factor equal to the ratio of the volumes of water that the vessel contains full, and when emptied out (a ratio of ca. 100) – rinsing three or four times should suffice to dilute to an insignificant level (one millionth, 10^{-6}), with a final rinse in pure water for sensitive kit. Consider if drying is really necessary before using a piece of glassware or equipment – the presence of a little more pure water will not matter if you are going to make up the solution to a prescribed volume, but drops of water will dilute a ready-made solution of pre-determined strength.

3.3 Chemical Measurements

First, let it be said that the New Chrysotype is a resilient process and works over a wide range of reagent concentrations. It is robust and forgiving enough to tolerate considerable variations and inaccuracies in preparation and measurement and yet still deliver acceptable results. This has become evident in recent years from the fairly successful attempts by imitators to replicate the process, without a proper knowledge of its quantitative chemistry. However, if you aspire to achieve the finest results, with a high degree of reproducibility and the maximum economy, then you should be prepared to make fairly careful measurements of the relevant quantities. The following instructions are written on that assumption.

3.3.1 Precision and accuracy

The hallmark of intelligent chemical practice is to work to a precision appropriate for the task – neither too low, nor too high. To assist you in deciding what precision is appropriate, the following notes attempt to explain some of the conventions of quantitative chemistry.

The abbreviation ‘ca.’ will be frequently encountered in this text. Sometimes just written *c.*, it is short for *circa,* the Latin for ‘about’. It does not have a generally accepted definition in scientific use, but may be taken here to imply that a precision in the order of ±10% is appropriate. E.g., a weight specified as ca. 30 g means any amount between 27 and 33 g should do; a temperature specified as ca. 50°C implies that any temperature between 45°C and 55°C would be acceptable.

In everyday scientific practice, the manner in which a numerical quantity is written makes an implicit statement about the precision to be observed in

measuring it experimentally. Generally, the precision should match the last significant figure, which has usually been rounded up or down. E.g: a weight specified as 30.0 g implies weighing to a precision of 0.1 g, i.e. the weight should lie between 29.95 g and 30.05 g. A weight written as 30 g implies a precision of 1 g, i.e. any weight between 29.5 and 30.5 g is acceptable.

When scaling quantities of substances, e.g. multiplying up volumes of solutions, keep in mind that the precision required is determined by the number of significant figures, not the number of decimal places. E.g., suppose a volume of 1.25 ml (measured with a precision of 0.01 ml) is to be scaled up by a factor of 10: this results in a volume of 12.5 ml (measured with a precision of 0.1 ml). In both cases, the precision of measurement is 1 part in 125 parts, or 0.8% (100/125 %).

3.3.2 Measuring volumes of liquids

Nearly all volumes of liquids quoted in this work are expressed in cubic centimeters, for which the approved symbol is cm^3 (often written elsewhere as cc). Occasionally, for specifying large volumes, it will be more convenient to use the liter, which is the same as a cubic decimeter:

$$1 \text{ litre} = 1000 \text{ ml} = 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

A measuring jug is usually accurate enough for dispensing volumes of water on this scale. Readers more familiar with the millilitre (ml) as a volume measure, may note that 1 ml is now defined as exactly the same as 1 cm^3.

The easiest method of accurately measuring the small volumes of liquid required in much of this work is by means of calibrated “disposable” plastic hypodermic syringes which are graduated with numerical volume markings. Most emphatically, these are ***not*** to be fitted with the hypodermic needles for which they were originally designed. Cheap, disposable plastic syringes are widely available from medical and laboratory suppliers (and can be used many times before they need to be discarded); capacities of 1, 2 or 2.5, 5, and 10 cm^3 will be found most useful. The precision of measurement is quite adequate, and the wastage of precious solutions is very small. Always use a syringe that is minimally larger than the volume you wish to measure, so as to maintain the maximum precision. E.g. to measure 0.75 cm^3, use a 1 cm^3 syringe, not a 5 cm^3 or 10 cm^3 size, which have coarser graduations.

Each sensitizer stock solution should have its own dedicated syringe(s) or pipette, which should be labelled on barrel and plunger to avoid cross-contamination (I use small self-adhesive coloured dots - green for iron, yellow for gold, etc). The method of use is as follows (figures 3.1-3.2):

1. Ensure that the plunger of the syringe is fully depressed.
2. Place the nozzle well below the liquid level in the bottle, and draw the liquid into the syringe by slowly withdrawing the plunger to a point *above* the desired volume.
3. With the syringe held vertically, nozzle down, over the bottle, gently expel the liquid until you reach the desired volume. Take the volume reading from the *bottom* of the *plunger*, not from the meniscus of the liquid.
4. Ignore the small air bubble that is present in the syringe between plunger and liquid. *Do not attempt to expel the air bubble*[32]
5. The ‘missing’ volume of liquid corresponding to the air gap is exactly compensated by the extra liquid contained within the uncalibrated tip of

the syringe, a volume which is included when practically all the liquid is expelled by the plunger, thus there is little or no waste by this method.

6. Wash out syringes thoroughly after use by pumping them in pure water, and pull the plunger out to dry separately from the barrel.

Figure 3.1. Draw liquid into syringe

Figure 3.2. Measure from plunger

A more expensive and fragile alternative for precise volume measurement is provided by graduated glass pipettes, especially the kind used in haematology, called serological pipettes, usually of 1 or 2 cm^3 capacity. These must be used with a pipette filler (a rubber bulb or piston type). Operation of pipettes by mouth is now strictly forbidden in all chemical practice.

Since the earliest days of alternative processes, in the 19th century, when calibrated equipment was less available, it became a common practice to measure small volumes of solutions in a relative manner only, by counting the number of drops from a dropping pipette or 'medicine-dropper' bottle. While this may be fairly consistent for the practice of a given individual, who always uses the same droppers in the same way with the same liquids, the volume of one person's drop may differ considerably from another person's drop, and errors are magnified in the counting.

For water, a drop defines a very approximate unit of volume of 0.05-0.06 cm^3 which apothecaries called a "minim". A rough rule of thumb is "about 17 drops to the cm^3 or ml". According to the physics of stalagmometry,[33] the volume of a drop is directly proportional to the surface tension of the liquid, (which can vary greatly - e.g. the surface tension of water is about 3x that of alcohols). Drop volume is also inversely proportional to the density of the liquid being dispensed. This means that different liquids (or solutions) give different sized drops - even with the same dropper - while It does also depend on the radius of the dropper

outlet, the material of the dropper tube, and the shape of the dropper tip. To try to measure precious metal solutions this way is scientifically -and economically- ridiculous. Dropping pipettes only have their uses, however, for making small additions where precision is low, e.g. for Tween20 wetting agent.

Graduated glass pipettes are the more sophisticated -and fragile- option for the chemically-trained, and require a mechanical piston or rubber bulb to suck up the liquid, because - whatever the historical traditions of chemical practice - pipettes today are never used by mouth, for safety reasons. The most convenient way of measuring out pre-set volumes of liquids are adjustable micropipettes with disposable slip tips.

Volumes of liquid larger than ca. 10 cm^3 are measured out with sufficient precision for our purposes by means of graduated measuring cylinders – in the USA these are curiously referred to as 'graduates'[34] The plastic type of measuring cylinder, which is familiar equipment to the dwindling breed of photographic darkroom worker, is adequate, but glass is preferred for better precision of measurement and susceptibility to more thorough cleaning. A good quality measuring cylinder of 100 cm^3 capacity is graduated so that it can be read to within 1 cm^3 - a precision approaching ±1%. Remember that the calibration marks on all volumetric chemical glassware are based on the rule of use that it is the *bottom* of the curved liquid meniscus that should just touch the calibration line (figure 3.3).

Figure 3.3. Measurement by meniscus.

3.3.3 Weighing solids

All weights in this work are expressed in grams, which are universally abbreviated as g. Never write this as 'gr', because it will cause confusion: in the old literature the abbreviation 'gr' signified the unit of 'grains', now long obsolete, and a much smaller measure (15.43 gr = 1 g).

Modern single-pan electronic scales working to a precision of ± 0.1 g are now inexpensive, and are ideal for our purposes, but there is nothing against the use of traditional beam balances, provided they have sufficient precision for the sensitizer formulae. For making up large quantities of

processing solutions, a precision of ± 1 g, obtainable with some kitchen scales, will usually serve. You should always protect the balance pans from direct contact with chemicals, which may corrode them, by containing the substance in a glass or plastic beaker. Alternatively, disposable containers may be used: a creased paper sheet will serve, but paper cupcake containers, plastic tubs, or cleaned yoghurt pots are less likely to lead to spillages. Small amounts of solid should be transferred using a spatula or plastic spoon. Remember to subtract the weight of the empty vessel or paper from the total. Many modern electronic balances or kitchen scales have a 'tare' facility which enables the scale reading to be reset to zero with the empty vessel *in situ*. The scale reading then gives the weight of the added material alone. Always ensure that the tare on such balances is reset to zero, with nothing on the pan, before you start a weighing.

3.4 Making up Solutions – Techniques of Filtration

When a solid has dissolved in water, or other solvent, there are usually density variations left as liquid strata, due to incomplete mixing: at the risk of stating the obvious, it is very important to stir the solution thoroughly to homogenise it, before dispensing any. For all sensitizer solutions it is very important to exclude any suspended particles of solid matter that could cause unwanted marks on the final print, so filtration is a standard procedure in the sensitizer solution preparations. Only the simplest apparatus is required: a conical filter funnel, made of glass or inert plastic. The size should be appropriate to the total volume of solution to be filtered – about a quarter to a tenth of that volume, because more solution is added little by little to the paper in the funnel as the filtration proceeds. The diameter of the filter paper chosen should be no more than twice the diameter of the funnel; use of an overlarge filter paper will cause a proportionally greater loss of solution due to absorption. The standard technique for folding filter papers is shown in Figure 3.4. Filter papers are manufactured in various grades for different purposes; generally, grade #1 is adequate for the solutions to be prepared here.

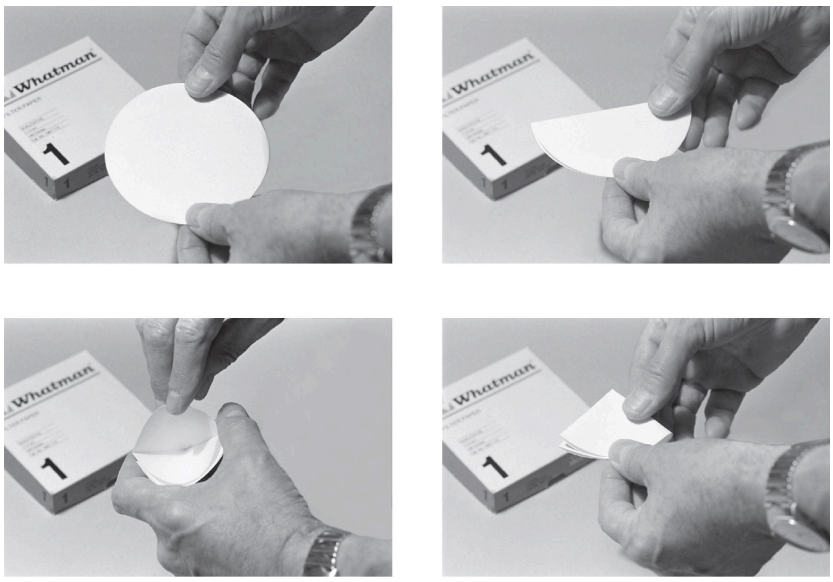


Figure 3.4. Folding a filter paper.

3.5 Expressions of Concentration

The concentration of a solution can be specified in a number of different ways, the choice of which will depend on whether the user is a chemist or not. Those who have studied early photographic literature will be aware of this diversity and the occasional difficulty in making comparisons, which is dealt with in Appendix III. Reconciling or interconverting these different modes of expressing concentration is not altogether trivial, and sometimes even impossible with complete exactness. Fortunately, high precision is not a prerequisite in this area. The only measures of concentration that need be considered for the current practice are as follows.

3.5.1 Concentration as weight percent volume (% w/v)

When a solution is said to have a concentration of C % w/v, this implies that C grams (g) of the solute are contained in 100 cubic centimeters (cm^3) of the solution. This measure of concentration only has meaning if the units are appropriately chosen – usually as grams per decilitre. (1 decilitre = 0.1 litre = 100 ml = 100 cm^3)[35] The convenience of this mode of expression is obvious, because solutions are most easily dispensed by liquid volume, and the measured volume (in decilitres) multiplied by the concentration, C, in these units provides an exact statement of the weight of solute (in g) that is present in the volume dispensed.

3.5.2 Concentration as weight percent weight (% w/w)

A concentration of C % w/w implies that C grams (g) of the solute are contained in 100 grams of the solution, or any other unit of weight for both.

3.5.3 Concentration as volume percent volume (% v/v)

A concentration of C % v/v implies that a volume of C cm^3 of the liquid solute are contained in 100 cubic centimeters (cm^3) of the solution, or any other unit of volume for both.

3.5.4 Concentration as Molarity

This is the 'chemist's unit' of concentration. A molarity of M, implies that the solution contains M gram molecular weights (or 'moles') of the solute in one litre of the solution.

A knowledge of molarities enables the chemist to predict exactly the equivalent combining volumes of solutions of reacting substances. Molarity is the basis for all analytical chemistry in solution, especially titrations.[36] Although its use is not necessary in everyday photographic practice, it is desirable to be able to calculate concentrations as molarities when devising new formulations, or reviewing old ones in which the level of chemical understanding may not have been accurate.

It is easy to convert the expression for concentration as C % w/v into the molarity, M, by multiplying by 10 and dividing by the gram molecular weight, R, (also called the relative molecular mass):[37]

$$M = 10\ C/R \text{ moles/litre}$$

R is found by summing the atomic weights of the component elements in the molecular formula, and values of R are given in the list of chemicals, see Appendix I.2.

3.5.5 Calculating dilutions

Occasionally it may be necessary to be able to calculate what volume of a concentrated solution must be added to a given volume of water, or other solution, in order to arrive at a desired final concentration of the substance in question. There is a very simple general relationship that enables such calculations, which follows from the fact that the total amount of substance (its 'weight', or more correctly mass) is unchanged in the process of dilution.

Since weight = volume x concentration

Or in more compact algebraic notation:

$W = V. C$

And if we represent the initial volume by V_I and initial concentration by C_I and final volume by V_f final concentration by C_f

Then it follows that if W is unchanged:

$V_I . C_i = V_f . C_f$

Provided the same units are retained throughout.

This equation may be re-arranged to give the desired unknown, which is often V_I

$V_I = V_f . C_f / C_I$

An example: what volume of 20% Tween solution must be added to 5 cc of sensitizer to give a final Tween concentration of 0.2%?

$V_I = 5 \times 0.2 / 20$

$= 0.05$ cc (approximately 1 drop)

This is an approximate calculation, valid when the added volume is small compared with the substantive volume, so the final volume is nearly the same (in this case 5.05 compared with 5.00).

If the added volume is comparable with the substantive volume V_s, the calculation is more complicated. The final volume is given approximately by:

$V_f = V_s + V_I$

From which it follows that:

$V_I = V_s . C_f / (C_I - C_f)$

3.6 The Choice of Gold Salt

Naturally, the gold compound is the most expensive component by far in the preparation of the sensitizer. There are at least three readily-available gold compounds to choose from, and the prices for these substances can vary quite widely, depending on the source. In setting out all the options, the following instructions seem more complicated than you need in practice. It is likely that you will find that hydrogen tetrachloroaurate is the least expensive option.

Although it has been advised that products of unnecessarily high purity should not be purchased, you may find the minimum purity of gold salts available is specified as 99.9% (which actually refers only to the purity of the metal content). On no account order salts of 99.99% purity or higher. A glance at the prices quoted in a catalogue will show you why. Note that CAS numbers differ with purity.

The theoretical gold content of these substances (Appendix II) is based on the formulae as quoted. However, their actual composition may depart from the idealised theoretical figure owing to variations in the quantity of water of crystallization in the batch. The better manufacturers provide an

analysis of the gold content – which is called the 'assay' – referring to the actual batch of chemical supplied. If the manufacturer's assay differs by more than 1 or 2% from the theoretical figure in the table, then in order to arrive at the correct concentration, a correction of the quantity of water used to make up the solution should be applied, as described below. If the salt you are using departs significantly from this content see the information in Appendix II.

Note that the gold contents of sodium tetrachloroaurate and hydrogen tetrachloroaurate are almost the same – to within 1%, so the quantities of these two can be used interchangeably. These gold chemicals are usually packaged by the supplier in small preweighed quantities, typically 1 g and 5 g, which may be taken to be accurate, although it is always worth checking, if you have the means. Otherwise, if you are weighing out the chemical from a larger stock, bear in mind that it is deliquescent and readily absorbs water from the atmosphere, gaining weight and ultimately dissolving entirely to form a solution. These gold compounds are corrosive and oxidising. They attack most metals and organic matter, and will stain your skin a spectacular purple. Do not use metal spatulas (stainless steel or nickel plated) to handle them, for they will be attacked. Inert plastic is best. Owing to their reactive properties, they are sometimes supplied in completely sealed glass vials. In case you are unfamiliar with handling such a container, here is a procedure for opening vials.

3.7 Opening Sealed Glass Vials

1. Soak off the label (if there is one) in cold water (but keep it).
2. Clean the outside of the glass vial (use alcohol or acetone to remove adhesive).
3. Gently tap the crystals to one end of the vial (if possible – but do not worry if they are too 'tacky').
4. Gently make a scratch with a glass-cutting knife or small triangular file at the centre of the vial, at right angles to the length of the tube, extending about a quarter of the way round the circumference.
5. If you have a gas torch available (or a plumber's blowtorch), melt a tiny red-hot blob of glass at the end of a very thin glass rod and 'spot' the scratch with it – this will cause a crack to run around the tube and make it very easy to snap open. If you do not have a burner, then you will have to take your chances with the following 'brute force' procedure.
6. Wrap the vial in a single folded piece of clean, strong card (this is to protect your fingers and catch any crystals of the salt that may fly out).
7. Hold the two ends of the wrapped vial with the thumb and forefinger of each hand and, with the scratch turned away from you, use a gentle bending action to snap the vial in two.
8. Carefully unfold the card.
9. Tip the loose contents of each half of the vial into the measuring cylinder, plus any crystals that have fallen out onto the card sheet.
10. Using a dropping pipette, add small portions of pure water to carefully dissolve and wash out any crystals still adhering to the inside of the vial halves, and transfer all the solution to the measuring cylinder. Repeat this until the wash water is no longer yellow.

11. If the glass vial shatters into pieces when you snap it – do not panic! (Some people prefer to open vials by smashing them.) Tip the entire heap of debris from the folded card into a small glass vessel or beaker. Add a small volume of water (about a quarter of the final volume to be made up), stir well to dissolve all the gold salt and transfer with a dropping pipette into the measuring cylinder – the transfer of a few glass fragments does not matter. Repeat with at least two more portions of water to wash out the gold solution.
12. Make up the solution in the measuring cylinder to the correct final volume.
13. Filter the solution directly into the clean stock bottle, using a small conical filter funnel and a small #1 Whatman filter paper.

4 New Chrysotype Processes

The new chrysotype sensitizer is unstable and must be prepared by mixing carefully-measured volumes of three or four stock solutions a few minutes prior to coating the paper. For brevity, the solutions required will be designated as: ***A. Ligand, B. Gold, C. Iron***, and ***D. Alkali***
This chapter describes three ways of formulating new chrysotype sensitizers which, for convenience, are called Versions '**S**', '**M**', and '**P**'.
These three differ in the following respects:

Version '**S**' (for the 'Sodium' method) is completely 'user-friendly', employs simple chemistry (a '3-bottle' mixture), and is quite safe to work. It is recommended for your first experience of gold printing.

Version '**M**' (for 'Methyl sulphoxide') is intended for the more experienced practitioner and offers the possibility of achieving even finer results with a higher degree of colour control. The price to be paid for this is a slightly more complex procedure for preparing the sensitizer, and a greater risk of damage to the negative. Version '**M**' only differs from '**S**' in one of the three component solutions of the sensitizer, the Ligand solution, **A**; the other two are the same, so it is easy to step from one procedure to the other.

Version '**P**' (for 'pH parameter') introduces an extra variable for the worker to experiment with - the pH, or acidity/alkalinity, of the sensitizer. Variations in pH influence the colour, contrast, and degree of printout. This is controlled by adding alkali, and involves the use of a more complex '4-bottle' mixing. The other three stock solutions are easier to make up than are those for '**S**' and '**M**', however, because they do not require neutralization. Version '**P**' is recommended for the experienced worker, who measures accurately and keeps careful records.

In the instructions that follow, you will find a number of options offered for making up the solutions, which are completely equivalent in their outcome, but may be adopted according to your local availability and price of the chemicals, especially the gold salt.

4.1 New Chrysotype Version 'S'

4.1.1 Chemicals required for the Version 'S' sensitizer

N.B. Only one name is used here for each of the requisite chemicals. For all their alternative names, and the properties and hazards of these chemicals, with suggested sources of supply, see Appendix I.

A. 3,3'-Thiodipropanoic acid
B. *EITHER* **B1. Sodium tetrachloroaurate(III)** dihydrate
OR **B2. Hydrogen tetrachloroaurate(III)** trihydrate
C. Ammonium iron(III) oxalate trihydrate
D. *EITHER* **D1. Sodium carbonate** (anhydrous)
OR **D2. Sodium hydrogen carbonate**
E. Tween 20™
F. Water (pure)

4.1.2 Chemicals required for processing

Developing agents; one or more of the following:
Disodium EDTA (1,2-Diaminoethanetetraethanoic acid, disodium salt)
Citric acid
Tartaric acid
Oxalic acid

Clearing agents:
Tetrasodium EDTA (1,2-Diaminoethanetetraethanoic acid, tetrasodium salt)
Sodium sulphite *OR* **Sodium disulphite** *OR* **Kodak Hypo Clearing Agent™**

4.1.3 Apparatus required for making up the sensitizer

(Figure 4.1)
One small Pyrex™ or Corning™ glass beaker (100-200 cm^3)
One graduated glass measuring cylinder (50-100 cm^3)
One large beaker or plastic measuring cylinder (ca. 500 cm^3)
One small conical filter funnel (ca. 5-6 cm diameter)
Filter papers: Whatman™ Grade #1, (ca. 8-10 cm diameter)
Two glass stirring rods, one long and one short.
Dropping pipette (2-3 cm^3 capacity) or small graduated syringe
Balance or scales accurate to ± 0.1 g, capacity at least 100 g
Electric hotplate/magnetic stirrer (or, simply a basin of hot water)
Spatula or small plastic spoon
Washbottle filled with pure water
Three brown glass bottles with plastic screw-caps, ca. 50 cm^3 capacity
Self-adhesive labels and indelible pen

4.1.4 Preparing stock solutions for Version 'S' sensitizer

A. Ligand solution (1.4 molar)

1. Weigh out 12.5 g of 3,3'-thiodipropanoic acid and transfer it into a beaker or measuring cylinder of ca. 500 cm^3 capacity (This vessel is necessarily large in order to contain the foam generated in the reaction that follows).

2. Weigh out separately ***ONE*** of the following (whichever is available):
   7.4 g of sodium carbonate anhydrous
   8.7 g of sodium carbonate monohydrate
   20.0 g of sodium carbonate decahydrate
   11.8 g of sodium hydrogen carbonate.

3. Add ca. 30 cm^3 of pure water to the thiodipropanoic acid and stir it into a suspension with a glass rod.

4. Slowly add the solid sodium (hydrogen) carbonate powder, in small portions of ca. 1 g, to the suspension of thiodipropanoic acid. There will be effervescence as carbon dioxide gas is evolved – this is harmless. The suspension will foam up, but it should be contained by the tall vessel. Stir well and allow the foam to subside between additions. The solution becomes cold, so may be slightly warmed in a bath of hot water to hasten the reaction. Continue until there is no further effervescence, leaving a colourless solution. A few residual solid particles do not matter.

5. Pour the solution into a small measuring cylinder (50–100 cm^3 capacity) and make it up to a final volume of 50 cm^3 with pure water from the wash bottle and mix well.

6. Filter the solution through a #1 filter paper directly into the stock bottle (this is a slow process because the solution is somewhat viscous.) This solution should keep well, if correctly made up. Label it with the date and the following:

New Chrysotype: Version 'S'
Solution A: Ligand
Disodium thiodipropanoate 1.4 molar

Preparing stock solutions for Version 'S' sensitizer

B. Gold solution (0.35 molar. 13.9% w/v)

EITHER B1

1. Carefully transfer or weigh out 5.0 g of sodium tetrachloroaurate(III) into a Pyrex glass beaker of 100 cm^3 capacity. Use a plastic spatula or spoon – this gold salt will attack stainless steel and nickel.

2. Add ca. 25 cm^3 of pure water at room temperature to the gold salt in the beaker. You should use some of this water to wash out and transfer any residual crystals of gold salt from your weighing bottle or vial, by means of a dropping pipette. With gentle agitation, all the solid will easily dissolve to a yellow solution at room temperature.

3. Filter the solution carefully into a measuring cylinder (50–100 cm^3 capacity) using a small conical filter funnel and a Whatman #1 filter paper, or equivalent.

4. Add pure water from the washbottle, a little at a time, to the filter-paper, allowing it to pass through to wash out most of the residual yellow solution, and to make up the final volume to exactly 36 cm^3 in the measuring cylinder. Mix thoroughly.

5. Transfer the solution carefully from the measuring cylinder to the stock bottle. This solution is stable indefinitely.
   Label it with the date and the following:

New Chrysotype: Version 'S'
Solution B: Gold
Sodium tetrachloroaurate 0.35 molar

Preparing stock solutions for Version 'S' sensitizer

B. Gold solution (0.35 molar)

OR B2

If hydrogen tetrachloroaurate(III) is less expensive or more readily available than the sodium salt, then you can make your gold solution from it, using the following procedure for neutralizing this acid with anhydrous sodium carbonate or sodium hydrogen carbonate:

1. Carefully transfer or weigh out 5.0 g of hydrogen tetrachloroaurate(III) into a tall measuring cylinder (100 cm^3 capacity). Use a plastic spatula or spoon – this gold salt attacks steel and nickel.

2. Add ca. 30 cm^3 of pure water at room temperature to the measuring cylinder. You should use some of this water to wash out and transfer any residual crystals of gold salt from your weighing bottle or vial, by means of a dropping pipette. With gentle agitation, all the solid will easily dissolve to a yellow solution at room temperature.

3. Weigh out (precisely, if possible) 0.673 g of sodium carbonate (anhydrous powder), ***OR*** 1.07 g of sodium hydrogen carbonate, using a chemical balance. If your balance is not this precise, the figures may be rounded up to 0.7 g or 1.1 g respectively.

4. Slowly add the sodium (hydrogen) carbonate in small portions (tip of a spatula), to the solution of chloroauric acid. There will be vigorous effervescence as carbon dioxide gas is evolved. The spray should be contained by the tall measuring cylinder. Swirl the solution, and continue adding the solid to completion and no further effervescence.

5. Add pure water from the washbottle to make up to a final volume of exactly 36 cm^3 in the measuring cylinder with thorough mixing.

6. Filter the solution carefully into the stock bottle through a small #1 filter paper to minimise the residual loss of solution. Label it:

New Chrysotype: Version 'S'
Solution B: Gold
Sodium tetrachloroaurate 0.35 molar

Preparing stock solutions for Version 'S' sensitizer

C. Iron solution (1.4 molar. 60% w/v)

The following procedure must be carried out under subdued indoor lighting (40 watt incandescent tungsten bulb at least 1.5 meters away), not daylight.

1. Weigh 30.0 g of ammonium iron(III) oxalate into a small Pyrex glass beaker of *ca.* 100 cm^3 capacity.

2. Add exactly 33.0 cm^3 of pure water (from a measuring cylinder) at room temperature to the salt in the beaker. Stir well with a small glass rod to dissolve the bulk of the solid. The solution becomes cold, so gently warm the beaker in a bath of hot water to assist dissolution.

3. Within 5 minutes the solid will have dissolved to form an emerald-green solution (any slight cloudiness from a few remaining fine crystals of impurity should be ignored). The solution should not need to be 'made up', but check that its total volume = 50 cm^3.

4. Filter the solution through a Whatman #1 paper in a conical funnel, directly into a clean, dry brown bottle.

5. Store this bottle in the dark at room temperature. If, after a few days, a few white needle-like crystals (probably of ammonium oxalate) have appeared, re-filter the solution to remove them. This solution is close to saturation, and if it is allowed to cool much below 20 °C (68 °F), some emerald-green crystals may slowly grow at the bottom of the bottle. Warm gently and swirl to re-dissolve these. Stored carefully at room temperature in the absence of light, this solution will keep indefinitely. Label it with the date and the following:

New Chrysotype: all Versions
Solution C: Iron
Ammonium iron(III) oxalate 1.4 molar

4.1.5 Mixing the sensitizer solution for Version 'S'

The primary control of contrast in this process is provided by the molar ratio of ligand : gold, which can be varied between 2 and 6. A 'standard' value of 4 is recommended for your first trials. The molar ratio of gold : iron is always 1. Given the concentrations of the solutions made up as above (the ligand and iron solutions have the same concentration, 1.4 molar, which is 4 times the concentration of the gold solution, 0.35 molar), this determines that the **volume ratios** for these three solutions, **A : B : C** to mix a 'standard' sensitizer must be:

Volume Ratios of Ligand : Gold : Iron = A : B : C = 4 : 4 : 1

However, these volume ratios can be varied between the limits:

A : B : C = 2 : 4 : 1 and 6 : 4 : 1

in order to vary the contrast. (Note that the first of these ratio numbers also tells you, conveniently, the molar ratio of ligand to gold). The values you prefer will be decided by your personal taste and the density ranges of your negatives, but here are some guidelines:

Lower ligand : gold ratios than the 'standard' value of 4 give less stable sensitizers, which will print faster, with a longer tonal range and higher maximum density, but they have a greater tendency to fog in the highlights and to decompose before coating.

Higher ligand : gold ratios than the 'standard' value of 4 give more stable sensitizers, which will print less rapidly, showing higher contrast and slightly lower maximum densities, with clean highlights.

There is no benefit in significantly increasing the proportion of iron (**C**) in the ratios, because this tends to cause 'blocking up' of tonal gradation in the shadows, 'bleeding' of gold pigment from overexposed regions, and lower maximum densities. However, a small excess of iron (**C**) does no harm.

The actual volumes of the solutions you need to measure out will, of course, depend on the total area to be coated, i.e. number and size of your coatings, the nature of your paper, and the ligand : gold molar ratio you have chosen. As a guide, typical figures are set out in Table 4.1 for making up 10 cm^3 of mixed sensitizer

Table 4.1. Solution volumes to make 10 cm^3 of sensitizer for **'S'** and **'M'**

Ligand : Gold Molar Ratio **R**	Volume of **A** Ligand (1.4 M) **A**=10**R**/(**R**+5)	Volume of **B** Gold (0.35 M) **B**=4**A**/**R**	Volume of **C** Iron (1.4 M) **C**=**A**/**R**
2	2.86 cm^3	5.71 cm^3	1.43 cm^3
2.5	3.33	5.33	1.34
3	3.75	5.00	1.25
4 standard	**4.44**	**4.44**	**1.12**
5	5.00	4.00	1.00
6	5.45	3.64	0.91

This is sufficient to coat about eight 10.25" x 8.25" (260 x 210 mm) areas of paper, on the assumption that each sheet requires ca. 1.25 cm^3 of sensitizer solution (which is true for Fabriano 5, HP 210 g/m^2 paper). For total volumes other than the 10 cm^3 used in this illustration, you should scale these numbers accordingly, selecting the row of volume figures, **A, B, C** that corresponds with your chosen ligand : gold molar ratio. For example, if you find that your chosen paper requires 1.6 cm^3 for each coating, and you wish to coat 8 sheets, then you will require 8 x 1.6 = 12.8 cm^3 of sensitizer, so each figure in the appropriate row should be multiplied by 1.28 to give the volumes to be measured out. These small volumes are conveniently and accurately measured out with the small graduated syringes, of capacity 1, 2, and 5 cm^3. It is good practice to dedicate a particular syringe to each solution, with an identifying mark, to avoid cross-contamination.
The solutions ***must*** be mixed in the following sequence:

1. Deliver the volume **A** of **ligand** solution into the mixing vessel using a graduated syringe (see Fig. 3.2).

2. Add the volume **B** of **gold** solution, drop by drop, from another syringe, with stirring or, preferably, careful swirling of the vessel (which avoids introducing a stirring rod). Allow time between each drop (1-2 seconds) for the gold solution to decolorise, and any precipitate to redissolve.

3. When step 2 is complete, add the volume **C** of **iron** solution, from a third syringe, to give a pale yellowish-green sensitizer.

4. Mix thoroughly and, using a fourth syringe, coat the paper sheets in the way described earlier in Chapter 2.

Although these volume figures have been quoted rather precisely, do not be daunted if you find it difficult to achieve this degree of accuracy in measurement: even with a calibrated syringe, you may have to guess the second decimal place. The process is quite forgiving over a range of values and you will obtain a result, albeit less predictable, with almost any reasonable combination of volumes.

The stability of the made-up sensitizer solution depends on the ligand : gold molar ratio and the temperature, but all solutions should last for at least 30 minutes at 20°C without showing any perceptible decomposition, which is sufficient time to coat a batch of sheets. The mixed solution cannot be stored; although the 'standard' solution should last at least 2 hours. Decomposition is indicated by the deposition of metallic gold, which plates the container.

4.1.6 Coating and drying

The method of coating the paper has been described fully in Chapter 2. If difficulty is encountered in achieving an even coating, a little Tween™ 20 may be added to the sensitizer to improve the absorption of the sensitizer by the paper fibres: 0.1-0.3 cm^3 of a 20% v/v solution, per 10 cm^3 of sensitizer solution, is appropriate (i.e. a final Tween concentration in the

sensitizer of 0.2 to 0.6%). Tween may also assist in 'smoothing out' the tones if a grainy or fibrous image is obtained, but it tends to be incompatible with gelatin-sized papers.

Immediately following the coating, allow the sheet to rest horizontally for a few minutes so that the sensitizer can soak into the surface fibres, as indicated by the disappearance of the reflective sheen. It may then be dried in a uniform stream of warm (40°C) air for about 10 minutes. After heat-drying, the coated paper may be stored in a light-tight desiccator at a Relative Humidity (RH) of 10% or less. The lifetime of prepared paper in storage is variable, depending on the parameters of the sensitizer. For preference, to avoid introducing this uncertainty, the paper should be exposed and processed on the same day that it is coated. If you adopt this as your method of working, then heat-drying the coating is not essential (unless you desire the result of a low RH): just leave it in the dark, e.g. in a drawer with plenty of air circulation to the environment, at room temperature for an hour or so, which suffices to reach equilibrium with the ambient RH.

4.1.7 Regulating the humidity of the paper

To attain a predictable result for the colour of the image, the water content of the sensitized paper must be controlled before exposure. Varying degrees of hydration will produce different colours in the print and different extents of printout: high RH generally yields a nearly complete printout in fairly neutral grey tones, or with a hint of blue or green. The lowest RH values give almost no printout: only the shadow tones are faintly visible, and the image is generated almost entirely by development, with pinkish-brown or dull red shadows and greyish-blue high values. The intermediate values of RH can provide strongly split-toned scales, with purple and magenta shadows graduating into blue highlights. This results from partial printout coupled with a some degree of development. Hydration can be controlled in two different ways, which will now be described. The first is simpler, but requires more attention because the process must be timed.

Water hydration chamber (time-dependent or kinetic method)

A heat-dried paper may be humidified over pure water, at 100% RH, for a timed period of up to 30 minutes, as described in Chapter 2. If the ambient temperature is much different from 20°C, then some correction to the time is necessary for consistent results. See Table A4.1.

Salt hydration chambers (equilibrium method)

These are chambers of known, constant RH, provided by saturated solutions of specified salts. Details of the construction and use of such enclosures has been described in Chapter 1. It is unnecessary to have a full range of RH chambers, however, and initially I recommend that you prepare just three, using the substances in Table 4.2.

These will convey some idea of the range of colour behaviour. Following that, the use of other RH values will be a matter of exploration and personal taste.

Table 4.2. Salts for the control of Relative Humidity atmospheres.

No.	Substance	Formula	RH%
H1	Calcium chloride, anhydrous	$CaCl_2$	9
H4	Calcium chloride, sat. aqueous	$CaCl_2$	32
H7	Sodium chloride, ditto	NaCl	75
or H8	Ammonium chloride, ditto	NH_4Cl	80

The RH box H1 can also be used for the storage of coated paper. Paper should be heat-dried before placing in this box, so as not to exhaust the desiccant too quickly. The RH box H4 can be made up using the spent calcium chloride from an H1 box, when it becomes too moist. A saturated solution is prepared, in contact with excess solid, in each case, as described in Chapter 2. Hydration in these chambers requires a minimum of half an hour, but papers may be left longer. The paper may tend to fog in the higher RH baths if it is left for much more than an hour, but if you intend to equilibrate at high RH, H7 or H8, the initial drying in hot air is unnecessary.

4.1.8 Exposure

Exposure times vary somewhat with the ligand : gold molar ratio, but are generally as short as for palladium sensitizers, for example. Using even modest UV light sources, adequate exposures may only be one or two minutes. The extent of printout is nearly total at high RH values, leaving less than 1 stop of development, but the printout decreases in the dried sensitizers, leaving 4 to 6 stops of development at the lower RH values. Test strips or step tablet tests are a useful guide in the latter case. The negative density range appropriate for a full tonal range in the print is indicated in Table 4.3 below, under 'controlling the contrast'. However, 'softer' negatives can still yield effective prints, especially if a high ligand : gold ratio is used.

4.1.9 Making up the processing solutions

Recommended Developer

Disodium EDTA, ca. 1% w/v solution: dissolve ca. 10 g (one rounded 5 cm^3 teaspoonful) in 1 litre of tap water at room temperature. Use this for a few prints only, in one session. Do not store it. Do not use tetrasodium EDTA instead, which may cause yellow staining.

Alternative Developers

Any of the following can be made up and used as 1-2% w/v solutions: tartaric acid; citric acid; oxalic acid. Because they are acids, overlong treatment may tend to block up the shadow tones, due to the coagulation of the gold, and better results may be obtained by using their sodium, potassium or ammonium salts.

These 'developers' should ideally all be employed as 'one-shot' process baths, or nearly so. Practically speaking, a 1 litre bath should be sufficient for 2 or 3 prints 10" x 8" or the equivalent area of smaller prints. It is risky to re-use these 'first bath' solutions, because they acccumulate most of the excess iron and gold salts, and soon acquire the ruby-red colour of colloidal gold which may cause staining of subsequent prints. Do not store these

solutions: make them up, ca. 1–2% in strength, as needed, by dissolving a rounded teaspoonful (8 cm^3) of the solid in one litre of water at 20°C.

Clearing Baths #I and #III

Tetrasodium EDTA, ca. 5% w/v solution: dissolve 50 g in 1 litre of tap water at room temperature. Two such clearing baths are required. They may be stored, and will have a capacity of around 50 10" x 8" prints per litre. It is economical to use '2-bath fixing procedure', by replacing the #I bath by the #III bath, when it is exhausted.

Clearing Bath #II

Sodium sulphite, sodium disulphite, or Kodak Hypo Clearing Agent: ca. 2.5% w/v: dissolve ca. 25 g (1 level 15 cm^3 tablespoonful of solid) in 1 litre of tap water at room temperature. This bath should not be stored, but made up fresh from solid for one day's printing.

4.1.10 Processing of the exposed print

1. POST-HYDRATE. This is an optional step in which the print is humidified, ***after*** exposure but ***before*** wet processing, by placing it in a water hydration chamber for a period of 2 to 15 minutes. The print is held parallel to and above, but out of contact with, the surface of water (larger than the print in extent). If the water is warmed to ca. 40°C the processing time can be shortened to 1–2 minutes, and the degree of development will be very complete. (A photographic dish-warmer serves well for this purpose. The arrangement is essentially the same as that for humidifier enclosures; for details see Chapter 2.)
   If you desire the lowest contrast, with the longest possible tonal scale, and the most delicate high values, then this procedure is strongly recommended. It allows the image to develop almost completely *before* it is immersed in the wet baths, which immediately start to wash out the chemicals. The hues are generally fairly monochromatic, i.e. without strong 'split tones', because of the lack of development. Post-hydration also yields very smooth tones. However, prolonged post-hydration can lead to chemical fogging of the image. Uniformity in exposure to the water vapour is important, and the humidifying tank should be kept in a draught-free location.
   A local, highly personalised, method of post-hydration is simply to exhale heavily on areas of the print where the fullest development is desired! (Like a Herschel 'Breath Print'. Do not allow lips to touch the surface!)

2. DEVELOP. One of the following 'developers' may be chosen, although 'development' is something of a misnomer here for the higher RH values, because the chief action of these baths is as 'clearing' agents. However, each does have a slightly different effect in 'fine-tuning' the resultant colour of the gold image. Vigorous agitation is important for the first couple of minutes. Prints may remain in this bath for up to 10 minutes.
   Water: this is the least 'energetic' option, and gives the greatest apparent contrast, because the high values may be truncated by lack of any developing agent.
   Disodium EDTA; 5–10 minutes gives a clean result with fairly neutral tones.

Tartaric acid; yields redder tones, but still fairly subdued.
Citric acid; from 1 to 6 minutes can produce a long tonal range of rose-pink hues crossing over into blue highlight tones if the sensitizer was exposed at low RH values. The intensity of the red colour in the shadows increases progressively with time and intensifies in the clearing baths. Overlong treatment may cause 'blocking up' of the shadows and a loss of tonal separation when the print dries down.
Oxalic acid; causes the most intense and striking red/blue colour splits and the longest tonal range.
These are not the only possibilities - the list of reagents could be very long - and opportunities for experiment are endless. The main criteria for selecting a chemical for the 'first bath' are: it should be a non-alkaline, non-reducing, chelating or complexing agent for ferric iron.

3. RINSE: thoroughly for half a minute in gently running water.

4. CLEAR #I: 10 minutes in a bath of 5% w/v tetrasodium EDTA, with only occasional agitation needed. Red tones will tend to intensify in this bath.

5. RINSE: briefly for a few seconds.

6. CLEAR #II: 10 minutes in a freshly-made bath of sodium sulphite or disulphite or Kodak Hypoclearing Agent of concentration ca. 2.5% w/v. Very little agitation needed.

7. RINSE: briefly for a few seconds.

8. CLEAR #III: 10 minutes in a second bath of 5% tetrasodium EDTA.

9. WASH: 30-60 minutes in gently running water.

10. DRY: Drain, face outwards, on a near-vertical sheet of glass, or Perspex™ (Plexiglass™ in the USA), for 10 minutes only, and then peg up on a line to air-dry, or place on a horizontal drying screen, of fine mesh to avoid drying marks. Alternatively, if cockling of the paper sheet is a problem, blot or roller it, and allow it to dry between sheets of high quality blotting paper, such as Multisorb, preferably under some pressure whenj it is uniformly dry.

4.1.11 Summary of steps in the New Chrysotype process

Step	Time/mins	Total time
1. Pre-hydrate paper [only if RH < 50%]		
2. Mark up for coating, and number the paper	1	1
3. Dust down paper and tape up for coating	1	2
4. Mix sensitizer [A:B:C = 4:4:1 standard]	2	4
5. Coat paper [5 passes] & blot off excess	2	6
6. Rest paper horizontally till sheen goes	5	11
7. Dry in warm air stream [40ºC]	10	21
8. Store in $CaCl_2$ [9% RH]	Indefinite time	
9. Hydrate @100% RH @ 20 ºC for timed period	0 to 15	36
…or using a constant humidity box	Indefinite time	
10. Register with negative in print frame	1	37
11. Expose to UVA light source	1 to 10	40
12. Post-hydrate @100% RH @ 20ºC	0 to 15	50
…or over water @ ca. 45 °C	1-2	
13. Develop in disodium EDTA [1%] or other	10	60
14. Rinse in running water	0.5	61
15. Clear #I in tetrasodium EDTA [5%]	10	71
16. Rinse briefly	0.5	72
17. Clear #II in sulphite or KHCA etc. [2.5%]	10	82
18. Rinse briefly	0.5	83
19. Clear #III in tetrasodium EDTA [5%]	10	93
20. Wash in running water	30	123
21. Drain on vertical Plexiglass™ sheet	15	138
22. Dry in air at room temperature and RH	Indefinite time	

4.1.12 Controlling the contrast

The contrast of the sensitizer is defined by its printing exposure scale, which is conveniently expressed as the negative density range, ΔD, from print highlight to deepest shadow. Control of this is achieved, as indicated earlier, by varying the molar ratio of ligand to gold, through the volumes and concentrations of the solutions **A : B.** A minimum value of molar ratio 2 gives the longest range of tones; however this ratio also corresponds to a very 'fast' and unstable sensitizer which tends to suffer fogging of the highlights. As the molar ratio is raised, the contrast increases as indicated approximately in Table 4.3 below; the performance also becomes more predictable; the clearing of the highlights is cleaner and the exposure times will require lengthening.

Table 4.3. Dependence of sensitizer contrast on ligand : gold ratio.

Ligand : Gold molar ratio:	2	2.5	3	4	5	6
Print exposure scale, ΔD:	2.8	2.4	2.2	2.0	1.8	1.6

4.1.13 Controlling the colour

The colour of a new chrysotype print depends on five main factors: the Version of the chemistry; the sizing agent in the paper; the humidity of the coating during exposure; and the developer used in the wet-processing procedure; additionally, the result depends on the acidity of the sensitizer: the pH is treated as a variable in Version **P** of the process, where it will be found that a more acidic sensitizer produces darker and duller reds with less printout.

Effect of the sizing agent

To obtain the best red and pink colours, choose a paper that has been tub-sized with gelatine, e.g. Fabriano 5, Arches Aquarelle, T.H. Saunders 'Waterford', or Bergger COT320. Alternatively you can surface-size papers yourself with gelatin as described in Chapter 2. Gelatin tends to stabilise and 'protect' the smallest particles of colloidal gold, which appear red. Tween20 surfactant also tends to promote red. For more neutral blue-black tones and dull magentas, the papers internally sized only with Aquapel™ may be used.

Hydration of the coating prior to exposure

The primary control of colour is the RH of the coated paper's environment at equilibrium before exposure. At low values (ca. 10%), the colours are predominantly pink and reddish-brown. As the RH is raised, the dominant colour shifts through magenta, via purple (45%), to bluish-black (80%). At high RH a fine range of grey/black tones is obtained, which compares very favourably with the best that the platinotype process can achieve.

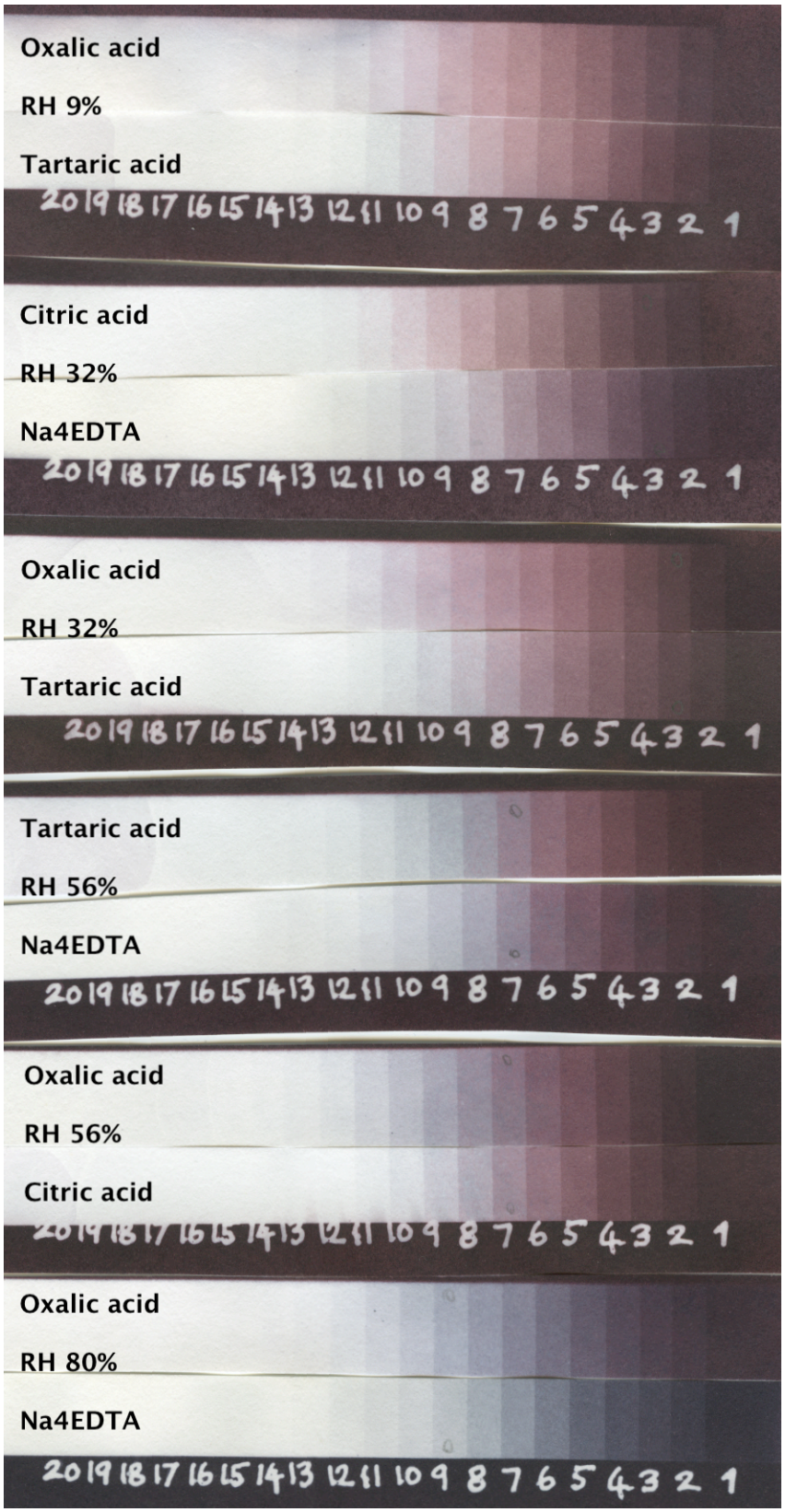
Choice of developing agent

The choice of 'developer' also influences the final colour, as outlined above: ranging from water through to oxalic acid. These developers act differently in conjunction with the RH. At low RH, citric acid produces pinks, and disodium EDTA browns, however at high RH citric acid produces bluish, and disodium EDTA greenish, results.

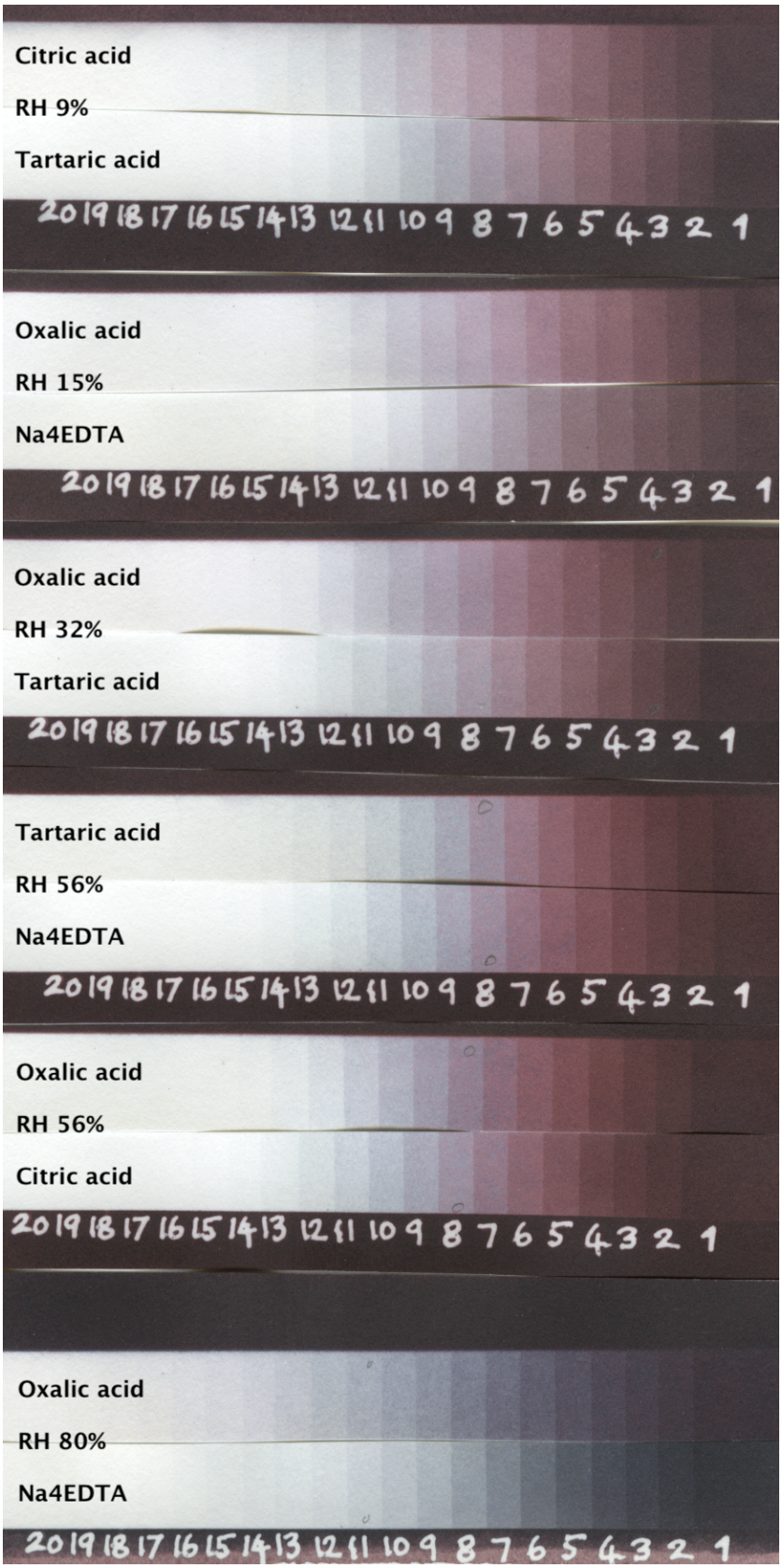
4.1.14. Results of Step Tablet tests on Version 'S'

Version 'S' on Fabriano 5. Na[AuCl4]

Final pH 4. Various developers and R.H. values.



Version 'S' on Fabriano 5. Acidic: H[AuCl4]
Final pH 2. Various developers and R.H. values.



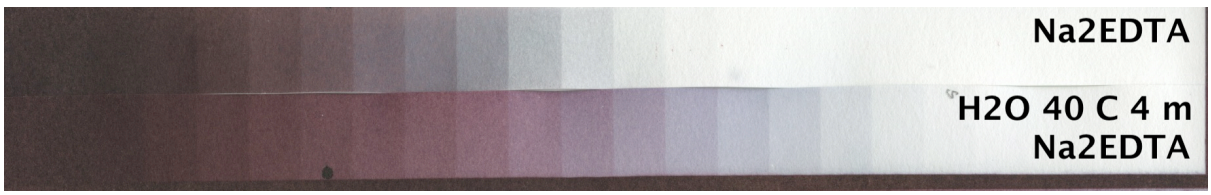
Version 'S': Ligand : Gold = 4 : 1
Kodak 3 Step Tablet on Fabriano 5 HP 210 gsm. No Tween

RH 9%. Post-hydrated and Na2EDTA developed

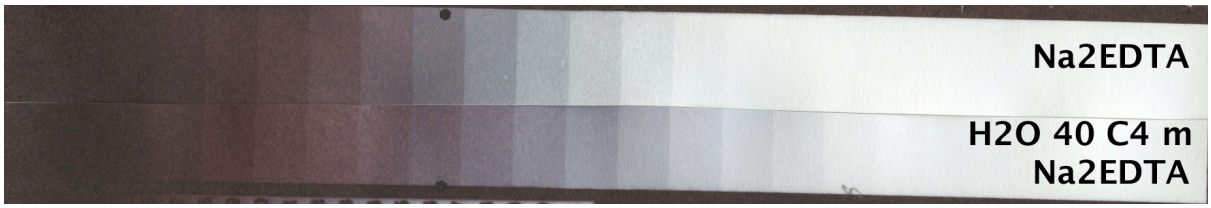
RH 32%

RH 80%

Version 'S': Ligand : Gold = 3 : 1
Kodak 3 Step Tablet on Fabriano 5 HP 210 gsm. Tween 0.8%



RH 9%



RH 32%

RH 80%

4.2 New Chrysotype Version 'M'

4.2.1 Chemicals required for the Version 'M' sensitizer

One chemical is required in addition to those specified for Version '**S**': **Dimethyl sulphoxide.** Tween20 is no longer required.

A. 3,3'-Thiodipropanoic acid
B. *EITHER* **B1. Sodium tetrachloroaurate(III)** dihydrate
OR **B2. Hydrogen tetrachloroaurate(III)** trihydrate
C. Ammonium iron(III) oxalate trihydrate
D. *EITHER* **D1. Sodium carbonate** (anhydrous)
OR **D2. Sodium hydrogen carbonate**
F. Water (pure)
G. Dimethyl sulphoxide

4.2.2 Preparing stock solutions for Version 'M' sensitizer

The gold and iron solutions, **B** and **C**, are identical with Version '**S**'. Only the ligand solution **A** differs in this version, made up as follows:

A. Ligand solution (1.4 molar)

1. Weigh out 12.5 g 3,3'-thiodipropanoic acid into a beaker of at least 250 cm^3 capacity (to contain the foam generated later).

2. Add exactly 16 cm^3 pure water from a measuring cylinder, and stir the suspension to a creamy paste with a small glass rod.

3. Add slowly, with constant stirring, exactly 25 cm^3 dimethyl sulphoxide from a measuring cylinder. The suspended solid will dissolve readily at room temperature, leaving a slightly 'milky' solution.

4. Weigh out 7.4 g anhydrous sodium carbonate, ***OR*** 11.8 g of sodium hydrogen carbonate.

5. Add the carbonate or bicarbonate powder a little at a time to the solution of thiodipropanoic acid. There will be effervescence and foaming, so stir well, until all the solid is added. Allow to stand until the sodium (hydrogen) carbonate has dissolved.

6. The final volume should already be correct = 50 cm^3; check if there may be need to 'make it up'.

7. Filter the solution directly into the stock bottle through a Whatman #1 filter paper (a slow process). Date and label it:

New Chrysotype: Version M
Solution A: Ligand
Disodium thiodipropanoate 1.4 molar, in 50% DMSO

4.2.3 Mixing the sensitizer for Version 'M'

The volumes to be taken and the mixing procedure are exactly the same as for Version 'S'. See Table 4.1

4.2.4 Differences in use between Versions 'M' and 'S'

Coating the paper

There are some small differences in behaviour between the two mixed sensitizers. The dimethyl sulphoxide in Version '**M**' is a penetrating agent that swells cellulose fibres. This greatly improves the absorption and smoothness of the coating using Version '**M**', and so makes the addition of a wetting agent or non-ionic surfactant like Tween 20 to the sensitizer quite unnecessary.

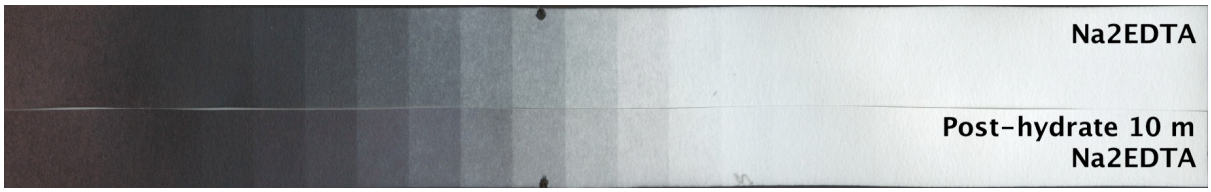
Drying

With Version 'M' sensitizer, it is usually necessary to heat-dry the coating because the dimethyl sulphoxide which it contains is extremely hygroscopic (i.e. it readily absorbs water from the atmosphere), and it may not dry out sufficiently at room temperature if the ambient RH is too high. Inability to dry will be evident from the fact that the coated paper does not lose its reflective 'sheen'. This version may be well-suited to very dry climates. If the coating is not heat-dried, then a thin polyester film barrier may be needed in order to avoid possible damage to negatives during contact printing. Dimethyl sulphoxide is employed in the Version 'M' sensitizer because it has the ability to wet and penetrate cellulose fibres to a high degree, which facilitates the saturation of the paper surface with sensitizer and provides a remarkably high maximum density. Its hygroscopic nature also ensures a much greater extent of printout, even at the lowest RH values, which consequently has a strong effect on the colours obtainable. The gradation of tones tends to be much more monochromatic with this sensitizer, and split-tones are not usually as conspicuous as they are with Version 'S'

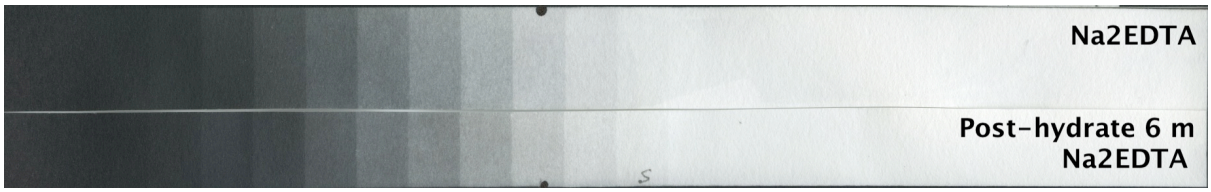
4.2.5 Results of Step Tablet tests on Version 'M'

Version 'M': Ligand : Gold = 3 : 1 pH 4.5

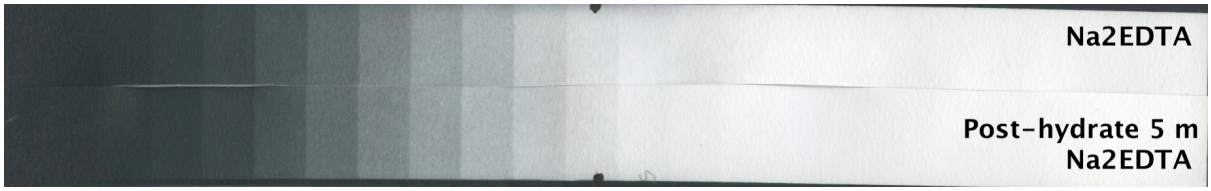
Kodak 3 Step Tablet on Fabriano 5 HP 210 gsm. No Tween



RH 9%. Not pre-hydrated



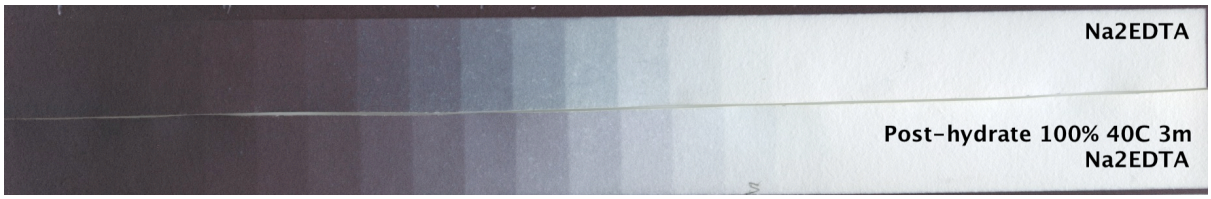
RH 9%. Then pre-hydrate 100% RH 22C 5 m



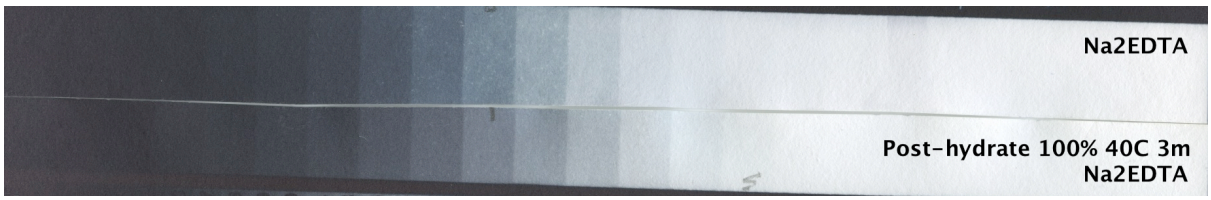
RH 9%. Then pre-hydrate 100% RH 22C 15 m

Version 'M': Ligand : Gold = 4 : 1 pH 5

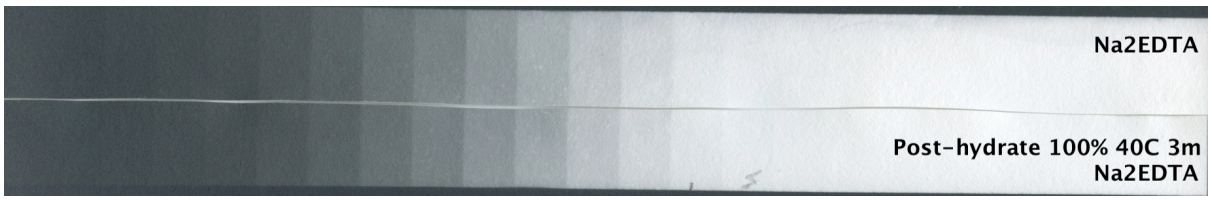
Kodak 3 Step Tablet on Buxton 160 gsm. No Tween



RH 9%



RH 32%



RH 80%

4.3 New Chrysotype Version 'P'

In this version use is also made of DMSO, but the ligand, **A,** and gold, **B,** solutions consist of the un-neutralised acids and are therefore simpler to make up than those in versions '**S**' and '**M**'. The iron solution, **C,** is the same as previously. A fourth stock solution, of sodium hydroxide, called **D3,** is additionally required, to adjust the pH of the mixed sensitizer, partially or completely neutralising the acidity.

4.3.1 Chemicals required for the Version 'P' sensitizer

A. 3,3'-Thiodipropanoic acid
B. Hydrogen tetrachloroaurate(III) trihydrate
C. Ammonium iron(III) oxalate trihydrate
D. Sodium hydroxide
F. Water (pure)
G. Dimethyl sulphoxide

4.3.2 Preparing stock solutions for Version 'P' sensitizer

A. Ligand solution (1.4 molar)

1. Weigh out 12.5 g of 3,3´-thiodipropanoic acid into a 100 cm^3 beaker.

2. Add exactly 16 cm^3 pure water from a measuring cylinder, and stir the suspension to a creamy paste with a small glass rod.

3. Add slowly, with constant stirring, exactly 25 cm^3 dimethyl sulphoxide from a measuring cylinder. The suspended solid will dissolve readily at room temperature, leaving a slightly 'milky' solution. Ignore the few particles left.

4. The final volume should already be correct = 50 cm^3; check if there may be any need to 'make it up'.

5. Filter the solution directly into the stock bottle through a Whatman #1 filter paper (a slow process). Date and label it:

New Chrysotype: Version 'P'
Solution A: Ligand
Thiodipropanoic acid 1.4 molar in 50% DMSO

Preparing stock solutions for Version 'P' sensitizer

B. Gold solution (0.35 molar)

NB This substance is highly corrosive.

1. Carefully transfer or weigh out 5.0 g of hydrogen tetrachloroaurate(III) into a Pyrex glass beaker of 50–100 cm^3 capacity. Do not use a metal spatula.

2. Add ca. 25 cm^3 of pure water at room temperature to the gold salt in the beaker. You should use some of this water to wash out any residual crystals of gold salt from your weighing bottle or vial, by means of a dropping pipette. With gentle agitation all the solid will dissolve to a yellow solution at room temperature.

3. Filter the solution carefully into a measuring cylinder (50–100 cm^3 capacity) using a small conical filter funnel and a Whatman #1 filter paper, or equivalent. Add pure water from the washbottle, a little at a time, to the filter, allowing it to pass through to wash out most of the residual yellow solution, and to make up the final volume to exactly 36 cm^3 in the measuring cylinder. Mix thoroughly.

4. Transfer the solution carefully from the measuring cylinder to the stock bottle. This solution is stable indefinitely. Label it with the date and the following:

New Chrysotype: Version 'P'
Solution B: Gold
Hydrogen tetrachloroaurate 0.35 molar
Danger: Corrosive!

C. Iron solution (1.4 molar)

This is the same as the iron solution **C** described above for Version 'S'.

Preparing stock solutions for Version 'P' sensitizer

D. Sodium hydroxide solution (14 molar)

NB **Eye protection is essential** in handling this substance.

1. Weigh out 28.0 g of sodium hydroxide pellets into a 50–100 cm^3 Pyrex glass beaker.

2. Add 30 cm^3 of pure water, and stir persistently with a glass rod to dissolve the solid. This may take some time, and the solution will become hot.

3. When all the solid is dissolved and the solution cool again, transfer to a 100 cm^3 measuring cylinder and make up to a total volume of 50 cm^3, mixing well.

4. Filter through a plug of glass wool or a hardened filter paper (The solution will attack a normal filter paper). Store in a plastic screw-cap bottle (NOT one with a ground-glass stopper, which will be attacked and become jammed.) This solution tends to absorb carbon dioxide from the atmosphere, so it should not be left unstoppered for any longer than necessary. Label it with the date and the following:

New Chrysotype: Version 'P'
Solution D3: Alkali
Sodium hydroxide 14 molar
Danger: Caustic!

4.3.4 Mixing the sensitizer for Version 'P'

When mixing the sensitizer for Version 'P' the same remarks regarding control of contrast apply, as with Versions 'S' and 'M'. However, both the ligand **A** and gold **B** solutions are acidic, so they are neutralized by the addition of an appropriate volume of the sodium hydroxide solution **D** *after* they have reacted; (the reaction itself produces more acid). The iron solution **C** must be added last.

The concentrations of the solutions made up as above determine that the **volume** ratios for these four solutions, **A : B : C : D,** to mix a near-neutral pH 'standard' sensitizer must be:

Volumes of Ligand : Gold : Iron : sodium hydroxide = A : B : C : D

A : B : C : D = 4 : 4 : 1 : 1.1

However, these volume ratios can be varied between the limits:

A : B : C : D = 2 : 4 : 1 : 0.7 and 6 : 4 : 1 : 1.5

in order to vary the final pH, and therefore the contrast.

The volume of sodium hydroxide (D) affects the final pH and the performance of the sensitizer. Less than the stated amount will lead to acidic sensitizers with less printout and duller reds. The sodium hydroxide may even be omitted completely, in which case the highly acidic sensitizer will not print out at all, and the image will be obtained entirely by development, and will be green in colour. In this case it is best to post-hydrate and develop in water only; other developers may fog the high values. The less acidic the solution is, the less stable it becomes. It is recommended that you do not use more sodium hydroxide than the stated amount, which should be regarded as a maximum, otherwise the iron solution may form a brown precipitate of ferric hydroxide.

Typical figures are set out in Table 4.4 for making up 10 cm^3 of mixed sensitizer, as before. For total volumes other than the 10 cm^3 used in this illustration, you should scale these numbers accordingly, selecting the row of volume figures, **A, B, C, D** corresponding with your chosen ligand : gold molar ratio.

Table 4.4. Solution volumes to make 10 cm^3 of sensitizer for Version **'P'.**

Ligand : Gold molar ratio	Volume of **A** Ligand (1.4 M)	Volume of **B** Gold (0.35 M)	Volume of **C** Iron (1.4 M)	Volume of **D** NaOH (14 M)
2	2.60 cm^3	5.19 cm^3	1.30 cm^3	0.91 cm^3
2.5	3.01	4.82	1.20	0.96
3	3.37	4.49	1.12	1.01
4 standard	**3.96**	**3.96**	**0.99**	**1.09**
5	4.42	3.54	0.88	1.15
6	4.80	3.20	0.80	1.20

The solutions ***must*** be mixed in the following sequence:

1. Deliver the volume **A** of **ligand** solution into the mixing vessel using a graduated syringe.

2. Add the volume **B** of **gold** solution, drop by drop, from another syringe, with stirring or, preferably, careful swirling of the vessel (which avoids introducing a stirring rod). Allow time between each drop (a few seconds) for the yellow precipitate to re-dissolve. The solution should now be perfectly colourless at this stage.

3. Next, carefully add the volume **D** of **sodium hydroxide** solution to the colourless solution formed in step 2, drop by drop, from a calibrated pipette or syringe. There will be no colour change, but a slight temperature rise due to the neutralization reaction – by about 6 to 8 Celsius degrees – allow the solution to cool before proceeding, by standing the vessel in cold water for a few minutes.

4. When step 3 is complete, finally add the volume **C** of **iron** solution, which should result in a very pale yellowish-green sensitizer.

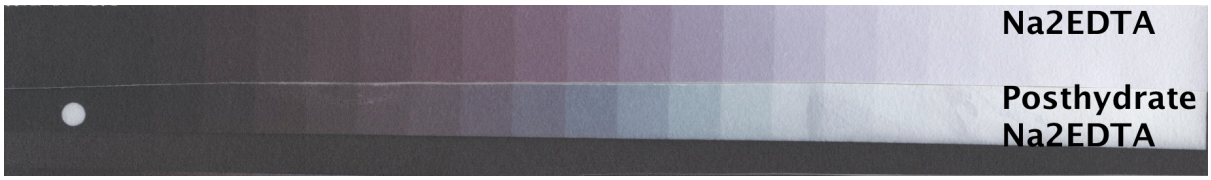
5. Mix thoroughly and, using a clean syringe, coat the paper sheets in the usual way and heat dry them.

The stability of the made-up sensitizer solution depends on the ligand : gold molar ratio, the temperature, and the pH, but all solutions should last for at least 30 minutes at 20 °C without showing any perceptible decomposition, which is sufficient time to coat a batch of sheets. The mixed solution cannot be stored; although the 'standard' solution should last at least 2 hours. Decomposition is indicated by the deposition of metallic gold, which plates the container.

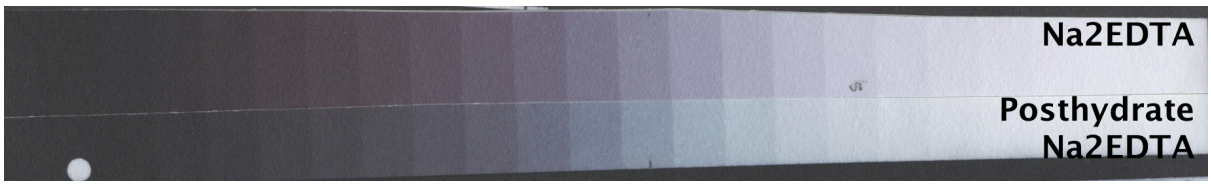
4.3.5 Results of Step Tablet tests on Version 'P'

Version 'P': Ligand : Gold = 3 : 1 pH 6.5

Kodak 3 Step Tablet on Buxton 160 gsm, CP. No Tween



RH 9%

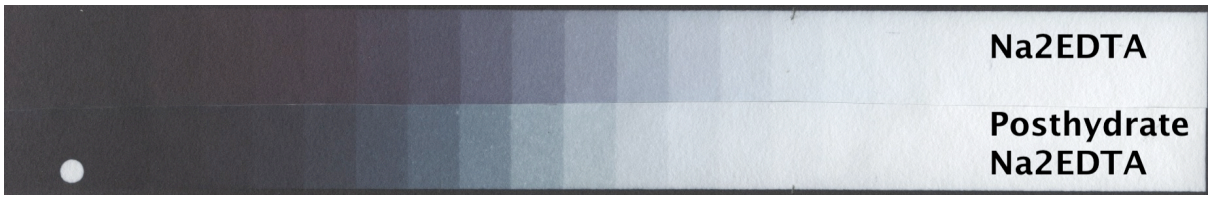


RH 32%

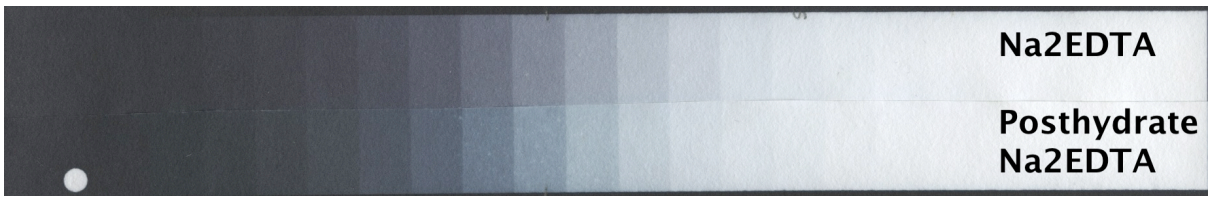
RH 80%

Version 'P': Ligand : Gold = 4 : 1 pH 7

Kodak 3 Step Tablet on Buxton 160 gsm, CP. No Tween



RH 9%



RH 32%

RH 80%

4.4 Intensification and Reduction of Chrysotypes

Gold images may be intensified by the selective deposition of more gold upon them from an inherently unstable solution of gold salts. This is called ‘electroless deposition’ or sometimes, inappropriately, ‘physical development’. The metastable solution contains a gold salt such as sodium chloroaurate together with a reducing agent such as hydroxylamine. If the state of aggregation of a colloidal gold image is altered, the colour will change and may appear more intense.
Chrysotypes may be intensified, with a substantial colour shift, by a 10% solution of methyl pyridinium chloride.

Although it takes a very powerful acid (aqua regia) to oxidise and dissolve gold in bulk, when it is in a finely divided state it may be dissolved by oxidation by air in the presence of ligands that coordinate very strongly with gold(I), especially cyanide, which is used in the commercial wet-extraction of gold from ores and residues. However cyanide is far too toxic for domestic use. A satisfactory safe ‘reducing’ agent for chrysotype images is provided by a mixture of thiourea (ca 2%) and citric acid (ca. 10%).

New Chrysotype Data Sheet

Date of coating		Version		Coat No.
Negative	D_{min}	D_{max}		Neg. No.
Title				
Paper		Weight	g/m^2	Surface
Pre-Hydrate	mins @	% RH @	ºC	
Molar Ratio Ligand : Gold =				

SENSITIZER		Conc/M	Vol/cm^3	Notes
A Ligand	Na_2TDP	1.4		
B Gold	$Na[AuCl_4]$	0.35		
C Iron	$(NH_4)_3[FeOx_3]$	1.4		
D Alkali	NaOH	14		
E Tween 20		20 %		

Ambient Temperature	ºC	Relative Humidity	%
Coating Volume	cm^3/sheet	No of Passes	
Coated Area x mm	Comments		

DRYING	Agent	T ºC	RH %	Time in	Time out	Date
Initial						
Store						
Hydrate						

EXPOSURE Light Source Time m s

PROCESS	Humidify	Develop	Clear #I	Clear #2	Clear #3
Agent	Water Vap		Na_4EDTA	$Na_2S_2O_5$	Na_4EDTA
Concn	100%RH	1%	5%	2%	5%
Time		10 min	10 min	10 min	10 min

NOTES

5 Negatives

The light sensitivity of siderotype papers like the chrysotype is about a million times less than that of silver-gelatine enlarging papers, so with the technology commonly available they cannot be projection-printed, only contact-printed to achieve a sufficient through-put of UV light. The reproduction scale of 1:1 leaves the photographer with four options:

- to make very small prints from conventional camera film negatives
- to work with a large format camera (not forgetting the 'pinhole' camera)
- to make enlarged internegatives photographically
- to make digital image files and output them as negatives with an ink-jet printer onto a translucent material.

Each of these strategies has something to recommend it, but whichever you adopt, it will be essential to produce negatives with a density range in the UV suited to the printing process.

[*Note added in 2021*: Some of the content of this chapter is now out-of-date because of the disappearance of many commercial silver-gelatin films from the market, but I let it stand in case their equivalents stage a comeback!]

5.1 Requirements for Suitable Negatives

The density ranges required in the negatives (ΔD) should be the same as the logarithmic exposure ranges (ΔlogH) of the iron-based sensitizers, because in contact printing there is no Callier Effect, where light-scattering enhances contrast. The ΔlogH values vary with process parameters, typically from about 1.5, equivalent roughly to a Grade 0 silver-gelatine paper, to a ΔlogH around 2.5, which is far softer than any silver-gelatin paper. As the Table 4.3 in Chapter 4 indicates, the 'standard' chrysotype process yields a range of ca. 2. log exposure units. To yield a full tonal range in the print, negatives must be made with a correspondingly long density range, from a typical 'film base + fog' value of about 0.2, to a D_{max} of ca. 2.2. The D/logH curves at the end of this section will be found useful in evaluating these printing ranges.

5.2 Development of Camera Films

To prepare suitable negatives directly from the camera film, as in the first two options, it should be given normal exposure (rating it at the manufacturer's recommended speed), but developed for 75% to 100% more than the normal time period recommended to produce a negative for silver-gelatine enlargement printing. Trial and error can be lessened by consulting the film manufacturers' published data for the variation of Contrast Index (Kodak's C.I. or Ilford's G) with development time or with developer concentration. As a guide, negatives for chrysotype printing should be developed to a C.I. value in the range 0.7 to 1.3, depending on subject and interpretation. These C.I. values are more or less incompatible with normal silver printing in an enlarger, so you cannot expect to use the same negative for both. However, in compensation, a negative prepared to this prescription will print well in all the iron-based processes: new cyanotype, argyrotype, platino-palladiotype, and new chrysotype.

A method for reconciling the incompatibility of the negative requirements for platinum and for silver printing has been advocated: namely, the use of pyrogallol as a developing agent. This not only reduces the silver halide in the usual way, but also stains the gelatin base yellow in the dense regions. This yellow stain does not add greatly to the optical density in the visible region, which determines the response of silver papers, but it does have a much enhanced absorption in the ultraviolet, which influences the response of iron-based papers. Thus one and the same negative can have different density scales in the visible and in the UV, and be compatible with both processes. Details of the preparation of 'pyro' negatives by the PMK formula can be found in a well-known monograph.[38]

5.3 Making Enlarged Internegatives

The third option offers a convenient compromise: to make your original negatives in the usual way for silver printing, ensuring adequate exposure to give plenty of shadow detail, and then to prepare internegatives of higher contrast from them. The user of 35mm and roll film formats is best advised to enlarge the original camera negative to give an internegative, which has the added advantage that the precious original is not put at risk by the rigors of contact printing. There are several ways to do this:

5.3.1 Direct duplicating film

Direct reversal duplicating (or diapositive) film makes a negative directly from a negative. A convenient (but expensive) method was to make internegatives by enlarging onto Kodak Professional Direct Duplicating Film Type SO-339, which later became SO-132 but is now discontinued; possible substitutes are provided by Agfa, who manufacture an aerial duplicating film Avitone PD3p or PD1p-OS, and Fuji, a medical duplicating film MI-DUP.[39] Dodging and burning may be carried out at this stage if desired. This film has orthochromatic sensitivity, so a red safelight is necessary.
N.B. These direct duplicating films are very slow materials and need heavy exposures under the enlarger. Even modest enlargements may require a minute's exposure at full lens aperture. Remember that they are reversal materials - more exposure produces less density. Remember always to make your internegatives as mirror images: i.e. place the original negative *emulsion up* in the enlarger so the duplicate will make a 'right-reading' image when exposed emulsion-to-emulsion on the print.

Very vigorous development is necessary to achieve an adequate maximum density in these materials. As a basis for experiment, if you are starting from ordinary negatives suitable for silver printing, develop the internegative in the Kodak high contrast developer D19 (undiluted) for 6 to 8 minutes at 22-24°C with continuous agitation. See the Kodak literature for further information.

5.3.2 Via an interpositive

The longer route is via an interpositive, using normal negative-working continuous tone films such as Kodak Gravure Positive Film 4135 or Agfa Gevatone N31p or N33p, which are available in large sheet sizes. This procedure represents a greater consumption of materials and time over the previous one. The choice of size for the interpositive will depend on your

available enlarger formats and budget, but to minimise the degradation in quality introduced by the extra copying step, and the problems introduced by dust, the larger you make the interpositive, the better. (Contact-printing an interpositive from a 35mm negative can introduce serious dust problems.) The interpositive should be printed quite heavily to ensure no loss of information; the highlights should appear somewhat grey and the tonal separation should still be visible in the shadows. Development to a Contrast Index value of one is recommended, and dodging and burning may be carried out at this stage so that the results can be readily judged. The negative is then made from this interpositive by enlargement or, preferably contact, onto the same film, using more vigorous development to raise the contrast. Kodak HC-110 is a convenient developer, offering control of contrast by varying concentration as well as time. Agfa market a continuous-tone orthochromatic sheet film, GO210p, which has the advantage of a variable contrast that can be adjusted by yellow or blue filters.

5.3.3 From diapositives

By starting with a positive transparency from the camera (such as Agfa Dia-Direct), an enlarged internegative can be obtained in one step on the films specified in 2. If the original small-format image is a colour transparency, projection onto these orthochromatic materials (which are insensitive to red light) will not faithfully reproduce the tonal balance. To maintain this, a panchromatic sheet film, e.g. Ilford's FP4 or HP5, will be necessary, possibly with a colour head or a filter to bring the enlarger light source to a daylight colour balance.

5.3.4 Paper negatives

Paper internegatives made under the enlarger from diapositives are a very economical but low-quality option. Obviously a thin-based paper stock will be needed to avoid long printing exposure times. The 'Resin-coated' (RC) variety is said to work well, and it has been suggested that the plasticised emulsion layer can easily be delaminated from the paper base by immersing the print in hot water at 46°C (115°F) for about three minutes, then teasing the layers apart at a corner with a fingernail, and slowly peeling away the backing paper, still under the water, but exactly which paper yields so easily is not disclosed.[40]

To avoid printing exposures becoming intolerably long, paper negatives may be 'waxed' to improve their translucency: the transmittance density of the paper substrate is thereby reduced from around 1.2 to 0.6, gaining two stops of exposure time. Beeswax dissolved in turpentine at a concentration of ca. 50% and used warm (50°C) is a convenient waxing agent, which penetrates the paper readily, then is blotted off and the turpentine is subsequently allowed to evaporate. Alternatively the undiluted beeswax may be 'ironed in' by melting between sheets of blotting paper, using a medium-hot domestic electric iron. The use of oils has also been advocated, but negatives thus treated tend to be messy to handle and impermanent under storage, and the print sensitizer must be protected.

Variations in paper texture, including any lettering on the back, can be cancelled out by giving a uniform white light exposure to the *back* of the photographic paper, in addition to the normal image exposure to the

emulsion side. A test strip is necessary to determine this additional compensating fog exposure, which will lengthen printing exposures.

5.3.5 Reversal processing

Conventional sheet film onto which a negative is projection-printed may be 'reversal-processed' to give another, enlarged negative directly. In a film that has been so exposed and developed to form a positive, but not fixed, the layers of silver halide that have not been developed into metallic silver are complementary to the layers of developed silver positive, and therefore represent an unexposed, undeveloped negative image. This would normally be removed by the fixing bath, but instead, the positive silver image is removed by a suitable 'bleaching' bath, after which the residual silver halide is fogged by light and developed to produce a negative.

Directions for carrying out this rather lengthy procedure, and the theory behind it, can be found in the standard photographic manuals. Kodak market a reversal-processing kit for their T-MAX films. Recently, reversal processing procedures have been devised for the inexpensive and widely available 'Lith' film, by Mike Robinson[41] and Liam Lawless,[42] with the specific objective of producing enlarged continuous tone internegatives with a long density scale suitable for alternative printing. A bare outline of the steps in this procedure is as follows:

1. Enlarge a continuous tone negative onto 'Lith' film: giving a heavy (3x) 'overexposure'
2. To restrain contrast in development, an overall flash exposure may now be given
3. Develop to produce a suitably high density range
4. Stop and rinse, and switch on a white light for the rest of the procedure
5. Bleach the silver image of the negative in 1% acidified dichromate solution
6. Wash, and clear in a 5% sodium sulphite bath to remove all chromate, and rinse
7. Illuminate, and redevelop the exposed residual silver halide completely
8. Fix (optionally) and wash.

Finding the appropriate exposures to provide the desired density range requires some careful making of test strips. The original articles should be consulted for details.

5.4 Use of Step Tablets

A chrysotype 'colour palette' may be made by using a small step tablet (Kodak #2 or a Stouffer) to print ca. 6 tests on a single 10 x 8 inch coated sheet, cut into strips, and variously processed at different, controlled RH values and/or with different developing agents (see §4.1.14).

If a densitometer is available to measure the transmittance densities of negatives to be printed – or even if they can be visually compared with a step tablet over a lightbox – such reference test sheets may be very helpful in suggesting the exposure and conditions needed to achieve a desired result from any given negative with the new chrysotype process. However, the density in the visible region of the spectrum is not necessarily a good indicator of the density in the ultraviolet, especially when the negative

pigment is an ink dye, which may have a varying spectral response, rather than silver particles.

5.5 Sensitometry

A large calibrated step tablet (Kodak #3) was used to generate specimen tests of the several versions of the New Chrysotype processes described in this work; their reflectance densities were measured using an X-rite densitometer, calibrated against a standard tablet, and their D/logH curves were plotted. For definitions in photometry and densitometry, refer to the Glossary.

5.6 Digital negatives

Thanks to the burgeoning industries based on semiconductor science, images may now be acquired electronically, either by scanning negatives or prints, or directly from a digital camera. Once stored in a computer as digital files, they may be extensively manipulated[43] and then output as large internegatives by means of a variety of high-resolution printing devices. This technology is improving so rapidly that anything written now will surely be obsolete by the time it reaches the reader. Even the modest 'domestic' personal computer now boasts sufficient memory storage and speed to handle the large (25-250 MB) files that represent high resolution images. Rather than offer detailed, machine-dependent procedures here which will rapidly become outdated, the state of the art at the the time of writing will be reviewed, and some general principles elucidated.

The first source on this topic for practising photographers was the book by Dan Burkholder *Making Digital Negatives for Contact Printing*.[44] At the time of its second edition (1999) the quality that a digital negative needed, to compare favourably with its photographic analogue, could only be achieved by employing professional machines – high resolution lithographic image setters – of the kind that are only affordable and operated by commercial print service bureaux. These are designed and intended for a different purpose than alternative print-making, so the negative data file in the computer must have a correction curve applied to it that is drastically non-linear, in order to make a data file that will produce an acceptable result from the imagesetter. These instruments also have the disadvantage that their scale of 'effective densities' often has a practical maximum D_{max} of 1.9 only, which is inadequate for the present methods of siderotype. In recent years, workers have sought alternatives to the ill-suited and expensive compromise of the imagesetter at the service bureau. The current trend – for obvious reasons of convenience – is towards perfecting the 'desktop negative', using for output an inkjet printer that is affordable by the private individual. The newer commercial models are now able to deliver sufficient resolution,[45] and Burkholder has up-dated his instructions accordingly in a supplement to his Manual, which is available for downloading from his website.[46]

Ink-jet printing onto ordinary acetate sheet is not satisfactory, but overhead projector transparency material has been developed with an absorbent coating of very fine transparent ceramic, such as Pictorico™ premium OHP transparency film, which allows quick drying and can hold

sufficient ink to provide the transmission densities needed in a printable negative.

The essential point to remember is that ***ink-jet negatives are completely different optically from the once-familiar negatives made with silver-gelatin emulsions***. The latter have a neutral density which does not vary much with wavelength: the density that is seen and measured in the visible region of the spectrum is a fairly accurate reflection of the density also present in the near UV, where the negative actually does most of its work when used for alternative printing. This is not so for digital negatives, which are made with soluble dyes or insoluble pigments, having absorbances in the near UV which can be quite different from their values in the visible region. Ordinary densitometers, which measure the visible wavelengths, are useless, and tell you nothing about the crucial values in the UV. If you are not fortunate enough to own a UV densitometer, or spectrophotometer, it is necessary to proceed empirically, as follows.

The full range of UV densities of the ink laid down on the transparency depends on three things:

- your particular make of printer
- the manufacturer's ink set
- the best choice of printer driver settings.

The Epson 'Ultrachrome'™ inks have been found to work very well, but there may be many other proprietory brands that are also suitable for alternative printing.The best printer driver settings can only be found and optimised by experimentally printing test negatives: we are, to an extent, at the mercy of these pre-set parameters, and can only judge by the way an ink-jet negative works in producing the final print. A driver setting is needed which will provide a UV ink density range equal to, or greater than the printing range of the process. This is usually found in the premium photo-quality settings for glossy or semi-glossy paper.

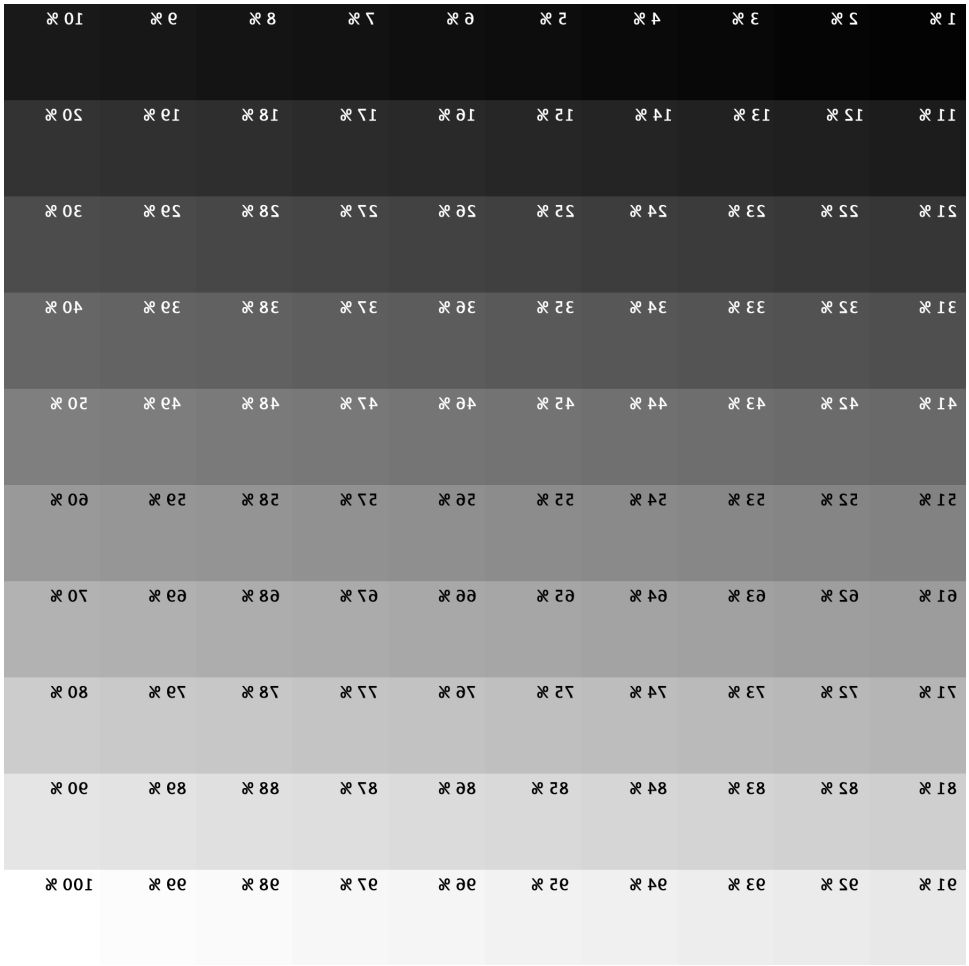
The first priority is to match the image ink density range of the digital negative to the exposure range of the printing process, so that an image region on the computer screen having an opacity value of 100% prints "just" white, and one of 0% opacity prints "nearly" the maximum density of the process (these opacity values refer to the negative image).

5.6.1 Calibration of the digital printing equipment and materials

We begin with a method of calibrating your individual digital system for the printer, ink set, driver software settings, and film substrate you actually use. Should any of these be changed, it will be necessary to re-calibrate.

This procedure uses a 100-step-tablet negative file (6.4 MB tiff) having intervals of 1% relative transmittance) as shown below.

It will provide internegatives suitably matched in their density range (at UVA wavelengths) to make contact prints having a full exposure scale in the chosen photographic process.



5.6.2 Procedure for carrying out the calibration

1) Load your printer with film identical that used for your negatives. Use the same ink set, and carefully record the printer driver settings. As a starting point, use the printer's 'premium photo-quality' media settings for glossy paper. All the colours of printer's ink-set are used, mixed in a smooth greyscale. The printer's driving software should include a control for adjusting the maximum ink density. Record its setting.

2) Output the digital file for the 100-step-tablet negative to your printer. Let this test negative dry and cure overnight before use, as inks have been observed to change density with time.

3) Assemble your usual print-making setup for your chosen alternative process, taking care that the light source, distance, and other conditions of printing, paper sensitising, and wet-processing are maintained consistently throughout.

4) Use your 100-step-tablet negative to make a trial contact exposure in your chosen process.
Increase the exposure if necessary, until you have a test print that is perceptibly overexposed, as judged by the criterion of shadow tones in the region of 99-95% negative transmittance beginning to 'block up' and become indistinguishable.
Call the exposure for this test print, E.

5) Examine the test print carefully when it is dry: the lowest part will appear dense and 'blocked up' with no resolution of the sequential steps. Now compare each step with the lighter one immediately *above* it - *i.e.* the one resulting from 10% less transmittance in the negative (which corresponds to a density difference of *ca*. 0.05, or one sixth of a 'stop'). Try to locate the first step, starting from the bottom, that is just perceptibly resolved in tone from the one above it; this lower step tells you the transmittance in this negative needed to produce your *effective* maximum print density. For brevity, call this transmittance P %.

6) Calculate your Standard Printing Exposure (SPE) by taking P % of E, the exposure for the test print made in 4):

$$SPE = E \times P/100$$

This SPE should apply approximately for all prints made in the chosen process, with your digital negatives, provided that the light-source and other printing and processing conditions are kept the same.
Note that the SPE is *not* sharply-defined, but can be varied a bit, because the *effective* maximum print density depends on how far up the shoulder of the characteristic curve of the chosen printing process you are prepared to place it. However, the higher you place your effective maximum density, the more of the 256 image levels you will need to allocate to increasing separation in the shadow tones, so you will have fewer left for the lighter tones of the image, and compress their contrast. Furthermore, if you seek to produce a 'maximum black' by extending the SPE excessively, the printer inks may not have sufficient UV blocking opacity to produce a 'paper base white' at all. In analogue photography, there is always a compromise, so try to *minimise your* D_{max} (!)

7) Using the Standard Printing Exposure, SPE, make a contact test print, in your chosen process, of the 100-step-tablet negative. Inspect the test print carefully, when fully dry, to find the step that appears 'just white' - *i.e.* the first one that has no upper boundary and which precedes the step with the first perceptible print tone.

8) If *no* steps print white, adjust your printer driver settings to lay down more ink when making the negative.
If several steps print white, you should adjust for less ink in the negative.

9) Go back to Step 2) and make a new 100-step-tablet negative, with the new settings, and re-test it through Steps 2) to 8). The ideal aim is to get 'just white' for the *first* step of the tablet - that having 1% transmittance or 99% opacity – but it should be satisfactory to get within 2 or 3 steps of this.

Experiment carefully with your printer driver settings: change the **maximum ink density** (a control usually found in the "colour management" window) and note its value when you make each new test negative. Print each one in your process with the same SPE until you come close to the ideal highlight tones. This is not a lengthy business; making four or five 100-step test-negatives at different ink densities will bring you close to the right ink density setting. These 100-step-tablets will, of course, be useful to calibrate any other process, which will, in general have a different exposure scale.

This concludes the calibration establishing the 'black and white' end-points for the exposure scale determined by SPE and Maximum Ink Density. You can now proceed to the Workflow.

5.6.3 Outline workflow for making digital negatives

Phase I: Acquisition of Digital Image File

1) Turn off colour management in photo software
2) Open image file – if already available, or –
3) Scan source – if necessary – and save

Phase II: Preparation of 'Perfected' Positive Image File

4) Preliminary image adjustments – if needed
5) Crop & re-size Image
6) Monochromatize – if an RGB colour image: L = 30%R + 59%G + 11%B
7) Burn & dodge – if desired (but a crude tool)
8) Set black & white levels
9) Adjust local contrast – in areas where needed
10) Retouch flaws – where necessary
11) Save 'perfected' positive image

Phase III: Preparation of 'Adjusted' Negative Image File

12) Apply a tone correction curve to the positive by resetting Gamma to ≈ 1.8 – 2.4 for desired contrast; this applies a suitable 'generic curve' automatically, making the negative's tonal scale appropriate for analogue printing (re-mapping it from a linear to a logarithmic scale)
13) Reverse handedness – if image reads correctly on screen
14) Invert tonality from positive to negative
15) Sharpen image with unsharp mask
16) Mask print border – if desired (but expensive in ink)
17) Flatten layers & save 'adjusted' negative image file

Phase IV: Printing the Negative Image File onto Transparency Film

18) Fine-tune negative opacity to match exposure scale
    If maximum ink density *cannot* give white for 1% step in (22):
    Adjust image layer opacity to the % opacity of the first 'white step'
19) Connect printer. Load Film & check ink levels
20) Select printer & page format setup
21) Reduce image file to 8 bits per channel if required by printer
22) Set printer driver & adjust maximum ink density to the value that gives ~1% transmittance in the negative printing as the 'white step'.
23) Output the negative
24) Number the negative & allow ink to cure.

Appendix I Chemical Resources

I.1 Description of Chemicals

The history of chemical nomenclature shows that substance names in the past were frequently idiosyncratic and irrational. The imprecision of using shortened 'popular' names for certain common chemicals has finally been resolved in recent years, but at a price. The recommendations of the International Union of Pure and Applied Chemistry (IUPAC) are necessarily intricate and – in spite of the name of that body – by no means universal in their acceptance and use. Chemical nomenclature confronts the lay person with a minefield to negotiate – even professional chemists find it tiresome, and most prefer to use the more concise and specific shorthand of chemical formulae. A unique and universal reference for most chemicals is provided by the registry number of the Chemical Abstracts Service, and is widely used in chemical catalogues. It is denoted in the lists below by CAS. If you are in doubt about the identity of a chemical from its name, then cross-check this number, but note that the same chemical in different states of purity may be designated by different numbers.

For the benefit of the chemically numerate reader, the molecular formula and relative molecular mass (denoted here by RMM, also known as the formula weight) are given in the lists below as a convenient reference for making your own calculations.

Regarding a suitable specification of purity for the chemicals, the grade known as GPR (standing for General Purpose Reagent) usually guarantees a purity in the order of 97–99%, and is adequate for our purposes. In the USA the term SLR is sometimes used (Standard Laboratory Reagent). Higher purity is, of course, acceptable, but will usually incur greater expense.

In the lists below, the corresponding catalogue numbers are quoted for the following major suppliers of fine chemicals, where appropriate:

Aldrich-Sigma Chemical Company Ltd
Alfa Aesar (A Johnson Matthey Company)
Bryant (A Spectrum Chemical Company)
Fluka (Riedel de Haën)
Merck (BDH)

Contact information for these companies may be found at the end of this Appendix.

The hazards associated with the chemicals listed are only briefly summarised below: the information has been abstracted from the published Materials Safety Data Sheets, which should always be consulted for more details. The hazards fall into three main categories:

Health: toxicity, or other threat as carcinogen or teratogen, when ingested or inhaled, or absorbed through the skin, and the risk due to direct contact causing corrosive damage to eyes, skin, or muco sa

Flammability: tendency to combustion

Reactivity: tendency to violent reactions with common materials: air, water, etc.

The two latter categories hardly apply to any chemicals used here.

I.2 Alphabetical List of Chemicals

Ammonium chloride

NH_4Cl
RMM = 53.49
CAS 12125-02-9
Aldrich #21,333-0 ; Alfa #12361, or #40193; Bryant #A335; Fluka #09700 or #09702 or #11212; Merck #159041 or #101141
Also known as: sal ammoniac.
Hazards: Harmful if swallowed. Skin, eye, and respiratory irritant.

Ammonium iron(III) oxalate trihydrate

$(NH_4)_3[Fe(C_2O_4)_3].3H_2O$
RMM = 428.07
CAS 13268-42-3; 14221-47-7
Aldrich #23007-3; Alfa #42112; Bryant #F335 (Spectrum #F1002); Fluka #12302; Citychemical #F393
Also known as: iron ammonium oxalate; ammonium ferric oxalate; ferric ammonium oxalate; ammonium trisoxalatoferrate(III) trihydrate.
Hazards: Harmful if swallowed, inhaled or absorbed through the skin. Corrosive – causes burns. Very destructive of mucous membranes. Toxicology not fully investigated.

Ammonium nitrate

NH_4NO_3
RMM = 80.04
CAS 6484-52-2
Aldrich #22,124-4; Alfa #12363; Bryant; Fluka; Merck #13,538
Hazards: Explosive if in contact with combustible material. Irritating to skin and eyes.

Ammonium oxalate monohydrate

$(NH_4)_2C_2O_4.H_2O$
RMM = 142.11
CAS 6009-70-7
Aldrich #37,974-3; Alfa #36228; Bryant; Fluka; Merck #13,541
Hazards: Harmful by inhalation and ingestion; causes severe internal pain.

Calcium chloride (anhydrous)

$CaCl_2$
RMM = 110.99
CAS 10043-52-4
Aldrich #22,231-3 ; Alfa #12316, or #33327; Bryant ; Fluka #21074 or #21079; Merck #102391 or #102379
Hazards: Harmful if swallowed. Eye, skin, and respiratory irritant.

Citric acid

$C(OH)COOH.(CH_2COOH)_2$
RMM = 192.12
CAS 77-92-9
Aldrich #25,127-5 or #C8,315-5; Alfa #31185; Bryant #C350; Fluka #27488 or #27109 or #03878; Merck #818707 or #100247
Also known as: 2-hydroxypropane-1,2,3-tricarboxylic acid; 2-hydroxypropane-1,2,3-trioic acid.
This substance is also obtainable as a monohydrate CAS 5949-29-1. Either form will do.
Hazards: Severe eye irritant. Skin and respiratory irritant. Prolonged or repeated exposure may cause allergic reaction in some individuals.

1,2-Diaminoethanetetraethanoic acid, disodium salt dihydrate

$C_2H_4(N(CH_2COOH)(CH_2COONa))_2.2H_2O$
RMM = 372.24
CAS 6381-92-6
Aldrich #25,235-2; Alfa #33312; Fluka #27285 or #03685 or #27270
Also known as: ethylenediamine tetraacetic acid, disodium salt; 1,2-diaminoethanetetraacetic acid, disodium salt; ethylenedinitrilotetraacetic acid, disodium salt; disodium edetate; sequestrene Na_2; disodium EDTA; Na_2EDTA.
Hazards: Harmful if swallowed; may be harmful if inhaled or through skin contact. Eye, respiratory tract and skin irritant.

1,2-Diaminoethanetetraethanoic acid, tetrasodium salt dihydrate

$C_2H_4(N(CH_2COONa)_2)_2.2H_2O$
RMM = 416.21
CAS 10378-23-1
Aldrich #E2,629-0; Bryant #E315; Fluka #03695; Merck #108436
Also known as: ethylenediamine tetraacetic acid, tetrasodium salt; 1,2-diaminoethanetetraacetic acid, tetrasodium salt; ethylenedinitrilotetraacetic acid, tetrasodium salt; tetrasodium edetate; tetrasodium EDTA; Na_4EDTA.
This substance is also obtainable as a tetrahydrate, CAS 13235-36-4. Either form will do.
Hazards: Eye, skin and respiratory irritant.

Dimethyl sulphoxide (sulfoxide in USA)

$(CH_3)_2SO$
(99% pure) N.B. Freezing point 18 °C (64 °F).
RMM = 78.13
CAS 67-68-5
Aldrich #M8,180-2; Alfa #16897; Fluka #41650 or #60153; Merck #802912 or #102952
Also known as: methyl sulfoxide.
Hazards: Skin, eye and respiratory system irritant. Readily absorbed through skin. Toxic if swallowed. Experimental tumorigen and teratogen. Reacts violently with a number of materials.

Hydrogen tetrachloroaurate(III) trihydrate

$H[AuCl_4].3H_2O$
RMM = 393.83
CAS 27988-77-8 (very high purity)
16961-25-4 (high purity)
16903-35-8 (acceptable purity)
Aldrich #24,459-7 or #25,416-9; Alfa #36400 or #12325; Bryant #G335; Fluka #50780 or #50790 or #12502 or #12503 or #50800; Merck #101582
Also known as: chloroauric acid; hydrochloroauric acid; auric chloride hydrochloride; gold(III) chloride hydrate, or, (in the earlier literature, which was ambiguous and inaccurate) as 'gold chloride'.
Hazards: Corrosive – causes burns. Extremely destructive of mucous membranes. May be harmful by ingestion or inhalation. May cause allergic skin reaction.

Iron(III) nitrate nonahydrate

$Fe(NO_3)_3.9H_2O$
RMM = 403.99
CAS 7782-61-8
Aldrich #21,682-8; Alfa #12226 or #33315; Merck #134057
Also known as: ferric nitrate nonahydrate
Hazards: Irritating to skin, eyes, and respiratory system. Harmful if ingested.

Oxalic acid dihydrate

$(COOH)_2.2H_2O$
RMM = 126.07
CAS 6153-56-6
Aldrich #24,753-7 or #O-875-5; Alfa #33262; Bryant #O226; Fluka #75702 or #27725; Merck #818242 or #100495
Also known as: ethanedioic acid.
Hazards: Harmful if swallowed, inhaled or absorbed through skin. Corrosive – causes burns. Very destructive of mucous membranes. May cause congenital malformation in the foetus: possible teratogen.

Sodium carbonate (anhydrous)

Na_2CO_3
RMM = 105.99
CAS 497-19-8
Aldrich #22,353-0; Alfa #11552; Bryant #S324; Fluka #71351 or #13418 or #71352 or #13419; Merck #159735 or #106393
Also known as: soda.
Hazards: Eye and respiratory irritant.

Sodium carbonate decahydrate

$Na_2CO_3.10H_2O$
RMM = 286.14
CAS 6132-02-1
Aldrich; Alfa #A17484; Bryant; Fluka; Merck
Also known as: washing soda
Hazards: Irritating to eyes. Ingestion of large amounts may cause nausea.

Sodium chloride

NaCl
RMM = 58.44
CAS 7647-14-5
Aldrich #22,351-4; Alfa #12314; Bryant #S328; Fluka #13423 or #71381; Merck #106404 or #159302
Also known as: common salt, table salt.
Hazards: May cause skin, eye, or respiratory irritation.

Sodium disulphite

$Na_2S_2O_5$
RMM = 190.10
CAS 7681-57-4
Aldrich #25,555-6 or #16,151-9; Alfa #33375 or #40115; Bryant #S342; Fluka #71930 or #13459; Merck #106528.
Also known as: sodium pyrosulphite, sodium metabisulphite.
Hazards: May act as an irritant or be harmful if swallowed. May act as an allergen in sensitive individuals.

Sodium hydrogen carbonate

$NaHCO_3$
RMM = 84.01
CAS 144-55-8
Aldrich #23,652-7; Alfa #14707; Bryant #S316; Fluka #71360 or #13433; Merck #106329
Also known as: sodium bicarbonate; bicarbonate of soda; baking soda.
Hazards: May irritate eyes .

Sodium hydroxide

NaOH
RMM 40.00
CAS 1310-73-2
Aldrich #22,146-5; Alfa #13455; Bryant #S350; Fluka #71692 or #06213; Merck #106482 or #159319
Also known as: caustic soda.
Hazards: Very corrosive. Causes severe burns. May cause serious permanent eye damage. Very harmful by ingestion. Harmful by skin contact or inhalation of dust.

Sodium oxalate

$Na_2C_2O_4$
RMM = 134.00
CAS 62-76-0
Aldrich #22,343-3; Alfa #41759
Also known as:
Hazards: Harmful by ingestion and inhalation. Irritating to skin and eyes. If swallowed causes severe internal pain followed by collapse.

Sodium sulphite

Na_2SO_3
RMM = 126.04
CAS 7757-83-7
Aldrich #23,932-1; Alfa #13454; Bryant #S360; Fluka #71991 or #13471 or #71990 or#13472; Merck #106657
Hazards: Possible mutagen. Harmful by inhalation, ingestion and skin contact. Eye, skin and respiratory irritant. Prolonged or repeated exposure may cause allergic reaction.

Sodium tetrachloroaurate(III) dihydrate

$Na[AuCl_4].2H_2O$
RMM = 397.8
CAS 13874-02-7
Aldrich #29,817-4; Alfa #84000; Fluka #12537
Also known as: sodium chloroaurate, sodium gold chloride.
Hazards: Corrosive. Destructive of mucous membranes. May be harmful by ingestion or inhalation. May cause allergic skin reaction.

L-(+) Tartaric acid

$(CH(OH)COOH)_2$
RMM = 150.09
CAS 87-69-4
Aldrich #25,138-0, T10-9; Alfa #30792; Bryant #T340; Fluka #95310 or #27504 or #27506; Merck #159472
Also known as: natural tartaric acid; L-2,3-dihydroxybutane-2,3-dicarboxylic acid.
Hazards: Skin, eye and respiratory irritant.

3,3'-Thiodipropanoic acid

$S(CH_2CH_2COOH)_2$
RMM = 178.21
CAS 111-17-1
Aldrich #T3,020-1; Alfa #A17220; Fluka #88600; Merck #808626
Also known as: 3,3´-thiodipropionic acid; thiodihydracrylic acid; diethyl sulphide 2,2´-dicarboxylic acid; bis(2-carboxyethyl) sulphide.
Hazards: Skin, eye and respiratory irritant.

Tween 20™

$C_{58}H_{114}O_{26}$
RMM = 1227.54
CAS 9005-64-5
Aldrich #27,434-8; Alfa #43309; Bryant #T355; Fluka #93773 or #63158; Merck #822184 or #817072
Also known as: polyoxyethylene (20) sorbitan monolaurate; Polysorbate 20™.
Hazards: eye irritant.

Water (pure)

H_2O
RMM = 18.016
CAS 7732-18-5
Purified by any suitably effective process (distilled, de-ionized, reverse osmosed), such as can be purchased from a pharmacist or obtained in any chemical laboratory.

I.3 Suppliers of Chemicals

This is by no means a complete list – there are many other sources of fine chemicals, too numerous to attempt to name them all here. Some of the major suppliers may stipulate a minimum order, or place restrictions on supplying chemicals to private addresses. Small amounts may be more conveniently purchased from photographic materials retailers who specialise in alternative processes, listed at the end of Chapter 1.

Sigma-Aldrich Co Ltd
The Old Brickyard
New Road
Gillingham
Dorset
SP8 4XT
UK

Tel: +44 (0)1747 833000 or 0800 717181
Fax: +44 (0)1747 833313 or 0800 378785
Email: ukpipeline@eurnotes.sial.com
http://www.sigma-aldrich.com

Alfa Aesar
Shore Road
Port of Heysham Industrial Park
Heysham
Lancashire
LA3 2XY

Tel: +44 0800 801812
Email: uksales@alfa.com
http://www.avocadochem.com/

Bryant Laboratory
1101 Fifth Street
Berkeley
CA 94710
USA

Tel: +1 510 526 3141 or 800 367 3141
Fax: +1 510 528 2948
Email: mark@bryantlaboratory.com
http://www.bryantlaboratory.com

Fluka (Riedel de Haën) obtainable from **Sigma-Aldrich**.

Merck (BDH)
Merck House
Poole

Dorset
BH15 1TD
UK

Tel: +44 207 669 700
Fax: +44 207 665 599
Email: info@uk.vwr.com
http://www.vwr.com

EMD Chemicals Inc.,
480 South Democrat Road
Gibbstown
NJ 08027
USA

Tel: +1 856 423 6300
Fax: +1 856 423 4389
Email: emdinfo@emdchemicals.com
http://www.emdchemicals.com

Appendix II Chemical Preparations

At the time of writing, all the chemicals needed for the New Chrysotype process can be bought 'off the shelf' from suppliers in Europe and the USA – and possibly elsewhere. However, if for any reason you have to make your own chemicals from simpler (and usually cheaper) starting materials, here are some preparative methods. It must be emphasised that these preparations should only be undertaken by those sufficiently skilled in chemical manipulations and who are well-acquainted with the chemical hazards.

II.1 Preparation of Ammonium Iron(III) Oxalate

If ammonium iron(III) oxalate is not readily available, a solution of it may be easily prepared by using the following procedure.

28 g of iron(III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$, in a pyrex vessel is gently heated to 50°C in a bath of hot water, until the pale purplish-brown crystals appear to 'melt' – actually they are dissolving entirely in their own water of crystallization – to give a deep red-brown solution. To this is added 30 g of finely powdered ammonium oxalate monohydrate (toxic: protect yourself with a mask against inhaling the dust), $(COONH_4)_2.H_2O$, with stirring at 50°C until all is dissolved to yield a clear emerald-green syrupy solution.

This solution can be used directly as a sensitizer without further purification: it must be diluted by adding water, to give a final volume of 50 cm^3 of a 1.4 molar solution of ammonium iron(III) oxalate (60% w/v). This solution will, of course, also contain excess ammonium nitrate at a concentration of 4.2 molar (34% w/v), which tends to deliquesce, attracting water into the sensitized paper. It therefore promotes the colours and contrast of the highly humidified papers – see below.

If it is desired to isolate the pure solid ammonium iron(III) oxalate, $(NH_4)_3[Fe(C_2O_4)_3].3H_2O$, the undiluted green syrup prepared above should be set aside in the dark to cool and crystallise. The fine emerald-green crystals of ammonium iron(III) oxalate trihydrate are filtered off and washed with methanol, in which ammonium nitrate, the by-product, is quite soluble. The product may be recrystallised from a water-ethanol mixture, (recrystallization from water-methanol tends to give a complex with methanol incorporated in the lattice). The solid should be dried in normal air and stored in the dark, (drying over anhydrous calcium chloride or silica gel will cause efflorescence and the loss of water of crystallization). The salt is very soluble, a saturated solution at 20°C having a concentration of ca. 1.4 molar.

II.2 Preparation of Hydrogen Tetrachloroaurate from Gold Metal

This is by far the most economical option, and can represent a cost-saving by a factor of ten, but it is a hazardous procedure, and should not be attempted by the inexperienced. Concentrated mineral acids are used, which are highly corrosive and evolve toxic fumes requiring proper safety precautions (eye protection and rubber gloves) and adequate facilities for

their dispersal. If carried out indoors, an essential requirement is an efficient laboratory-type fume-hood, with an extract suitable for dealing with corrosive vapours. This is not a process that is suitable for a domestic environment. It can be performed fairly safely on a small scale out of doors, in the right circumstances. You should not attempt this procedure unless you are familiar with handling concentrated mineral acids and confident that you can carry it out with minimal risk to yourself, other people, and the environment.

Even 'scrap' gold can be used provided it is of a reasonably high gold content - preferably 22 carat, but no less than 18 carat. (Pure gold is specified as 24 carat, so these varieties are 92% and 75% gold, respectively.) Even supposing that you can afford it, do not attempt to dissolve more than 10 g of gold at one time. Additives, accounting for the last two carats may be silver or copper. Any silver will be precipitated as the chloride during the procedure, and may adhere to the gold metal and inhibit its dissolution. Any copper present will be evident by its colour, which will impart a green tint to the solution. If the presence of copper(II) is undesirable, the product must be purified by re-precipitating gold metal by means of oxalic acid, filtering, washing, and re-dissolving.

The acid used to dissolve metallic gold is still known by its alchemical name, *Aqua Regia,* which translates rather appropriately as 'royal water', for it is the only common acid capable of dissolving the most 'noble' of metals: gold and platinum. This reagent was also referred to in the last century as 'nitromuriatic' or 'nitrohydrochloric' acid.

II.2.1 Aqua regia

One volume of concentrated nitric acid[47] is mixed with three volumes of concentrated hydrochloric acid.[48] (older recipes give the volume ratio of the two acids as 1 + 4, respectively, which is close to a molar ratio of 1:3). An equilibrium is set up between these two acids and their reaction products, nitrosyl chloride, chlorine and water, which is usually written as:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$$

But the rate of establishment of this equilibrium is slow - taking maybe 24 hours, depending on the temperature. Both nitrosyl chloride and chlorine are gases, but somewhat soluble in water. If this mixture is kept in an open vessel at room temperature, the gases are slowly evolved and the reaction goes over to the right hand side of the equation above.[49] This decomposition is accelerated by heat: On warming aqua regia, an orange-yellow mixture of chlorine and nitrosyl chloride gases is evolved.[50] Further, nitrosyl chloride is itself unstable in water, but it only decomposes slowly to give nitric oxide and chlorine:

$$NOCl + H_2O \rightarrow HNO_2 + HCl \rightarrow NO + {}^1/_2\, Cl_2 + H_2O$$

So the overall, long term decomposition of aqua regia can be represented as:

$$HNO_3 + 3HCl \rightarrow NO + {}^3/_2\, Cl_2 + 2H_2O$$

i.e. the acid becomes more dilute with time, and evolves noxious gases.

However, if the aqua regia is contained in a closed vessel, the red liquid phase (due to NOCl) will be in equilibrium with the gases above it, which will

exert some pressure. This pressure will increase steeply with temperature, as the equilibrium goes over to the right hand side of the equation above. Regarding this pressure, the recommendation is: "if aqua regia is to be stored for any length of time, the formula should include 1 volume of water, without which objectionable quantities of chlorine and other gases are evolved."[51] My recommendation is ***never*** to store aqua regia and only to make up sufficient for the task in hand. Any acid excess to requirements should be neutralised with chalk or soda lime before disposal.

II.2.2 Dissolution of gold in aqua regia

The textbooks rarely quote an equation for this reaction, probably because of the uncertainty regarding which of the several possible reduction products of nitric acid is actually formed; however, if we assume that it is entirely nitric oxide, (which seems to be supported by observation) then a simple equation can be written, for the formation of tetrachloroauric acid:

$$Au + HNO_3 + 4HCl \rightarrow H^+ + [AuCl_4]^- + NO + 2H_2O$$

i.e. 1 mole of gold liberates 1 mole of colourless NO gas, which becomes brown nitrogen dioxide, NO_2 on contact with the oxygen of the air:

$$NO + {}^1/_2 O_2 \rightarrow 2NO_2$$

There must be sufficient ventilation to allow these fumes to escape to the open air and not build up in the workplace.[52]

A quantitative point: the equation implies that one mole of gold requires (ideally) 4 moles of hydrochloric acid, HCl (plus the excess nitric acid) for its dissolution. The typical sample of 10 g of gold (0.05 moles) would therefore require, ideally, 0.2 moles of HCl, which is contained in ca. 18 cm^3 of concentrated hydrochloric acid, a volume which would be present in 24 cm^3 of 'standard' aqua regia. However, if this amount only were used, the rate of dissolution would probably become extremely slow towards the end, so this is a theoretical lower limit for the quantity needed. Typically, 40 cm^3 to 50 cm^3 of aqua regia are used to dissolve this amount, 10 g, of gold, which is ca. 100% excess acid. Use a pyrex glass beaker for the dissolution, heating if necessary to start the reaction, and ensure that the toxic brown fumes are safely dispersed.

When dissolution is complete, the excess acid should be fumed off, by evaporating down to a small volume. If any silver is present it will be converted to insoluble silver chloride, which is filtered off at this point – but it can adhere to the metal and inhibit dissolution in the first place. Excess nitric acid is 'chased out' by adding a little more hydrochloric acid and re-evaporating to a syrup, but not quite to dryness, until the chloroauric acid begins to crystallize. It is important not to overheat it, because the product tends to decompose at temperatures over 120° C.

II.2.3 Gold assay

Each gram of pure (100%) gold should be made up to a final volume of 14.5 cm^3 for a 0.35 molar solution of hydrogen tetrachloroaurate. When dissolving any gold compound, there is a simple formula for calculating the final volumes of such solutions - all the sensitizers in this work call for a stock gold solution of the same concentration, 0.35 molar. If the assay of the

compound is A% gold, and the weight taken is W g, then the final volume of solution, V, that it should be made up to, in order to obtain a solution of concentration 0.35 M, is given by:

$$V = 0.1451 \times A \times W \text{ cm}^3$$

e.g. 5 g of sodium tetrachloroaurate that assays at 49.5% gold should be made up to:

$$V = 0.1451 \times 49.5 \times 5 = 35.9 \text{ cm}^3$$

36 cm^3 would suffice for this precision.

Name	**Formula**	**RMM**	**% Gold**
Gold	Au	196.97	100.00
Sodium tetrachloroaurate	$Na[AuCl_4].2H_2O$	397.80	49.51
Hydrogen tetrachloroaurate	$H[AuCl_4].3H_2O$	393.83	50.01
Ammonium tetrachloroaurate	$NH_4[AuCl_4]$	356.82	55.20
“ “	$NH_4[AuCl_4].H_2O$	374.84	52.55
Calcium tetrachloroaurate	$Ca[AuCl_4]_2.6H_2O$	825.79	47.70
Potassium tetrachloroaurate	$K[AuCl_4]$	377.88	52.12
“ “	$K[AuCl_4].H_2O$	395.90	49.75
“ “	$K[AuCl_4].2H_2O$	413.91	47.59
Gold(III) chloride	Au_2Cl_6	606.66	64.93
Gold(III) oxide	Au_2O_3	441.93	89.14
Gold(III) hydroxide	$Au(OH)_3$	247.99	79.45

Table II.1. Gold content of commonly available gold compounds

Appendix III Reference Data on Obsolete Units

When interpreting 'historic' formulations, it is advisable to convert all units of weight to grams (g), and all volumes to cubic centimeters (cm^3). To assist this, the following conversions may be useful.

III.1 Weight

Apothecaries' measure was used by early scientists for weighing out solids and making up formulae:

1 grain		= 0.0648 g
1 scruple	= 20 grains	= 1.296 g
1 drachm	= 3 scruples (60 grains)	= 3.888 g
1 ounce	= 8 drachms (480 grains)	= 31.104 g
1 pound	= 12 ounces (5760 grains)	= 373.242 g

Troy weight has the same basis as Apothecaries measure, the grain, and was used for weighing precious materials such as gold and silver metal:

1 grain Troy	= 1 grain Apothecaries	= 0.0648 g
1 pennyweight	= 24 grains	= 1.555 g
1 ounce	= 20 pennyweights (480 gr)	= 31.104 g
1 pound	= 12 ounces (5760 grains)	= 373.242 g

The 'carat' ('karat' in the USA) was used to denote the number of parts of gold by weight per 24 parts of metal or gold alloy. Thus, 24 carat gold is 100%, 12 carat is 50% gold. [Confusingly, 'carat' can also denote a unit of weight for precious stones, where 1 carat = 0.200 g]

Avoirdupois measure was the common system for weighing and selling solids; it was adopted by the British Pharmacopoeia in 1864:

1 grain	= 1 grain Apothecaries	= 0.0648 g
1 ounce	= 437.5 grains	= 28.3495 g
1 pound	= 16 ounces (7000 grains)	= 453.592 g

The larger units in the Avoirdupois system – stones, quarters, hundredweights, and tons – are omitted as irrelevant here. Texts do not always make clear which system the 'ounces' (abbreviated 'oz.') in their formulae refer to, but they are more likely to be Avoirdupois, unless the substance is metallic gold or silver, when Troy ounces are appropriate. As a consequence of this ambiguity, an 'ounce' of silver nitrate weighed less than an 'ounce' of silver metal! Avoirdupois measure also defined a "dram" (usually so spelt to distinguish it from the Apothecaries drachm) of 1/16 ounce.

III.2 Volume

British fluid measure was used for measuring volumes of liquids. The Imperial pint of 20 fluid ounces replaced the ancient 16-ounce pint in 1826:

1 minim (ca. 1 drop)			= 0.0592 cm^3
1 fluid drachm	=	60 minims	= 3.552 cm^3
1 fluid ounce	=	8 fluid drachms	= 28.413 cm^3
1 gill	=	5 fluid ounces	= 142.065 cm^3
1 pint	=	20 fluid ounces	= 568.261 cm^3
1 quart	=	2 pints	= 1136.522 cm^3
1 gallon	=	8 pints	= 4546.087 cm^3

1 fluid ounce of water weighs approximately 1 ounce avoirdupois.
Many C19th workers described solution strengths in grains per fluid ounce:
A concentration of 1 grain/fluid ounce = 2.28 g/dm^3 = 0.228 % w/v
A unit of volume occasionally used was the cubic inch = 16.387 cm^3

The US system differs from British liquid volume measurement, and retains a 16-ounce pint:

1 minim (USA)			= 0.06161 cm^3
1 fluid dram (USA)	=	60 minims	= 3.697 cm^3
1 fluid ounce (USA)	=	8 fluid drams	= 29.574 cm^3
1 pint (USA)	=	16 fluid ounces	= 473.176 cm^3
1 gallon (USA)	=	8 pints	= 3785.412 cm^3

III.3 Specific gravity

This was commonly used to indicate the strength of some concentrated solutions, because these could be readily determined with a hydrometer or areometer. Unfortunately the scale often employed was the now long-obsolete (and ambiguous) **Beaumé hydrometer scale**.
For liquids denser than water, the number on the Beaumé scale, 0, 1, 2, 3, etc., denotes the specific gravity of aqueous solutions containing 0, 1, 2, 3, etc., % w/w of sodium chloride (common salt). If B represents the Beaumé number, and D is the specific gravity (or density in g/cm^3) as above, the relationships between them are:[53]

$$D = 1/(1- B/m)$$

or, conversely:

$$B = m(1- 1/D)$$

where the parameter, m, has been historically assigned various values between 144 and 147 on slightly differing definitions of the scale, (146.78 is the value taken for the Gerlach scale), but may be taken approximately as m = 145 for nineteenth century measurements at 20°C.

III.4 Concentration

Concentration as weight percent volume (% w/v)
If a solution is specified as having a concentration of C % w/v, this implies that C grams (g) of the solute are contained in 100 cubic centimeters (cm^3) of the solution. This measure of concentration only has meaning if the units are appropriately chosen – usually as grams per decilitre. (1 decilitre = 0.1 litre = 100 ml = 100 cm^3)[54] The convenience of this mode of expression is obvious, because solutions are most easily dispensed by liquid volume, and the measured volume (in decilitres) multiplied by the concentration, C, in these units provides an exact statement of the weight of solute (in g) that is present in the volume dispensed.

Concentration as weight percent weight (% w/w)
If a solution is specified as having a concentration of C_W % w/w, then C_W grams of the solute are contained in 100 grams of the solution (and likewise for any other unit of weight). Since it is much less convenient to measure and deliver samples of solutions by weight, rather than by liquid volume (a balance is much more costly than a measuring cylinder or pipette), this is a less practical mode of expression. The only advantage is its independence of the units of weight used, provided they are both the same; i.e. no units need to be specified, and it is also independent of temperature.

Concentration as volume percent volume (% v/v)
If a solution is specified as having a concentration of C_V % v/v, then a volume C_V cm^3 of the solute is contained in 100 cm^3 of the solution. This is obviously a useful measure when the solute is commonly obtained in liquid form.

III.5 Early formulations and recipes

Most of the older formulations and recipes for making-up historic photographic preparations usually prescribe a procedure of the form:

'Dissolve X parts (by weight) of the solute in V parts (by volume) of water (or other solvent).'

While it is easy to specify and carry out the making-up of a solution in this way, it also creates a quantitative difficulty, because the dissolution of the solute in the solvent changes the total volume, so that the solution finally obtained no longer has a volume equal to V, but one that has been increased (usually) by an unspecified and unpredictable amount that depends on the individual chemical identity of the solute. Only for dilute solutions, say 1% or less, is it a reasonable approximation to assume that V remains unchanged, and that the concentration may therefore be taken as % w/v, once the units have been converted to g/100 cm^3.

The concentration of a solution made up in such a way can be calculated exactly as C_W % w/w by:

$$C_W = 100\ X/(X + V\ d)$$

where d is the density (or specific gravity) of the solvent in appropriate units. If the solvent is water at room temperature, the assumption that d = 1 g/cm^3 is generally accurate enough, so the expression may be simplified to:

$$C_W = 100\ X/(X + V)$$

provided that X is expressed in g and V in cm^3.
Unfortunately, if a solution is made up in this way it becomes impossible to relate its concentration accurately to the more useful, rational, and chemically significant units of C % w/v, unless further information – the density – is available (see below).

III.6 Modern formulations and recipes

Most practising photographers have some experience in making up solutions for darkroom work,[55] and will be aware that the instructions in modern formularies now tend to take the form:
'Dissolve X g of the solute in water (an approximate volume may be indicated as a guide) and make up the solution with water, with thorough mixing, to a final volume of V cm^3.'
It is obvious that this way of making up solutions can be accurately expressed by a concentration of C % w/v simply defined by:

$$C = 100\ X/V\ \text{g/decilitre}$$

This method is greatly to be preferred, especially if quantitative chemical reasoning is to be employed, and it is also the way of working that is natural for any trained chemist.

III.7 Interconversion of C_W and C

The information needed to relate values of C_W and C is the specific gravity or density, D, of the solution in appropriate units:

$$D = C/C_W\ \ \text{g/cm}^3$$

In general, information regarding the density, D, of a solution of any particular strength is not readily available, although it has been tabulated for aqueous solutions of a limited number of common chemicals in the CRC Handbook, for example.[56] However, tables of *solubility* in the Merck Handbook[57] do provide values of C, C_W, and D for *saturated* solutions of quite a large number of substances, at room temperature.

Appendix IV Chemistry of Siderotype Printing

IV.1 Iron-based Photochemistry

In contrast to the halides of silver, there are no commonly available salts of gold (or the other noble metals) that are sufficiently photosensitive for direct image-making. An indirect route into noble metal imaging is therefore necessary, which is provided by the well-known photochemistry of certain iron(III) carboxylates.[58] The action of light on iron(III) (previously called 'ferric') salts of these organic acids produces iron(II) (previously 'ferrous') salts, by promoting an internal oxidation-reduction reaction by electron transfer. All the iron imaging systems have this same basis; the key compound is usually an iron(III) salt of either citric, tartaric, or oxalic acid.[59] For simplicity in the chemical formulae and equations, we will take the last-named as our example: ferric oxalate, which contains iron(III), Fe^{3+}, and oxalate, $C_2O_4^{2-}$, chemically bound together. Under the influence of ultra-violet light, this salt undergoes the reaction first observed in it by Döbereiner in 1831. Iron(III) reacts with oxalate under UV light to form iron(II) and carbon dioxide gas – a process which can be expressed by the chemical equation:

$$h\nu + 2Fe^{3+} + C_2O_4^{2-} \rightarrow 2Fe^{2+} + 2CO_2$$

UV light + iron(III) cations + oxalate anion → iron(II) cations + carbon dioxide

Note how two negative charges (which are carried by electrons) have been transferred from oxalate to iron(III), *reducing* it to iron(II). A similar light-induced change occurs in ammonium iron(III) oxalate, in which case the overall reaction can be more fully represented as:

$$h\nu + 2[Fe(C_2O_4)_3]^{3-} \rightarrow 2[Fe(C_2O_4)_2]^{2-} + 2CO_2 + C_2O_4^{2-}$$

UV light + trisoxalatoferrate(III) → bisoxalatoferrate(II) + carbon dioxide + oxalate anion

which acknowledges the complexity of the chemical species involved. The quantum yield (see Appendix V) for this process in aqueous solution is approximately one, per mole of iron for UV light of wavelength 365 nm. This reaction is accompanied by only a slight colour change from pale yellow-green to pale yellow-brown; moreover this change is temporary, because the iron(II) is slowly re-oxidised back to iron(III) by oxygen in the air.

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$$

iron(II) cations + oxygen + water → iron(III) cations + hydroxide anions

In order to make a permanent photograph, the iron(II) which is formed by the action of light must be immediately reacted to produce a more visible and enduring substance for the image. Chemically, the resulting iron(II) complex is quite a strong reducing agent, as may be seen from its redox potential:

$$E^o([Fe(C_2O_4)_3]^{3-}/[Fe(C_2O_4)_2]^{2-}) = +0.02\ V$$

because it readily gives up an electron and reverts to iron(III); so one option is to use it to reduce the compounds of 'noble' metals, such as platinum, palladium, silver or gold, to the metallic state, which then constitutes the final image, [60] *e.g.*:

$$[MX_4]^{2-} + Fe(II) \rightarrow M + Fe(III) + 4X^-$$

noble metal complex + iron(II) complex → noble metal + iron(III) complex

This is the general chemical principle underlying the historical 'iron-based' alternative printing processes in gold, silver, mercury, platinum and palladium, which correspond respectively to Herschel's original *Chrysotype,*[61] *Argentotype and Amphitype,*[62] which used ammonium iron(III) citrate as the photosensitive component, and to the later *Platinotype* and *Palladiotype* processes due to Willis,[63] which used iron(III) oxalate.

However, this second, image-forming reaction cannot take place in the dry sensitized layer, because the molecules cannot encounter one-another. They only achieve the necessary mobility if there is some water present; they can then react to form nanoparticles of noble metal which are trapped in the paper fibers to constitute the final image. If the sensitized layer is very dry, this water will be supplied by the first processing solution, and the image will be developed; however, some degree of printout will occur if the sensitized paper is not fully dried, but allowed to acquire a controlled degree of humidity prior to exposure. Under these conditions the gold image is formed during the exposure in a printing-out process, and may require little or no development afterwards, as is more fully discussed below.

IV.2 Choice of the Photosensitive Iron(III) Salt

There are a number of practical considerations affecting the choice of iron(III) carboxylate for use in the sensitizer. Ammonium iron(III) citrate, whose light sensitivity was originally discovered by Herschel, suffers from an extreme variability of composition, to the extent that it is described by chemists as 'ill-characterised'; meaning that it cannot be crystallized, but is only obtained as amorphous solids, with iron content ranging from 14% to 28%, and colours ranging from green to brown. The properties of this compound are more fully described in my book on Cyanotype.[64] The fact that this substance is not reproducible, and cannot be represented by one formula, is a strong disincentive to its use for any process demanding a degree of chemical precision, because no two workers can be sure that they are using the same material. It also has the disadvantage of being rather less photosensitive than the iron(III) oxalates, and poorly absorbed by cellulose.

The time-honoured substance, used in several siderotype processes such as classic platinotype and kallitype, is iron(III) oxalate. Unfortunately, this too is another of the compounds of iron which are stigmatized by chemists as 'ill-characterised'. Different preparative methods yield significantly different products, having the formulae $Fe_2(C_2O_4)_3.XH_2O$, where X is variously 4, 5, or 6. Despite being represented thus, it is certainly not a simple salt, but probably has several complex, oligomeric structures. Only one of these, for X = 4, has been subjected to X-ray methods of structure determination. The structure is polymeric, composed of zig-zag chains in

which the octahedral Fe(III) centres are bridged by cis-bidentate oxalate ligands, and these chains are cross-linked into a 2-dimensional layer structure by the third trans-bis-monodentate oxalate ligand; each Fe(III) centre also carries one coordinated water molecule to complete its octahedral coordination sphere. The two remaining lattice water molecules are hydrogen-bonded within the unit cell. Moreover, some forms of solid iron(III) oxalate can be very difficult to dissolve in water, and even when persuaded into solution there is a greater tendency for it to decompose over a relatively short time, providing a poor shelf-life.

Ammonium trisoxalatoferrate(III) also known as ammonium iron(III) oxalate, by contrast, is a model compound: it is easily obtainable in a pure, highly crystalline form, with a definite formula $(NH_4)_3[Fe(C_2O_4)_3].3H_2O$ and well-established molecular structure; it is completely reproducible, and has the added merit of a very high solubility in water to give a solution which is stable for years, but very light sensitive. When incorporated in a gold, or platino-palladiotype sensitizer, ammonium iron(III) oxalate readily provides a full print-out under humid conditions, which iron(III) oxalate – in any of its forms – does not. Ammonium iron(III) oxalate also has the advantage of being more readily removed from the paper by wet processing, so it is less liable to suffer the hydrolysis causing a yellow stain of residual iron - a common failing of many prints made with iron(III) oxalate.

Ammonium iron(III) oxalate was once an important commercial chemical for the coating of blueprint papers. Its availability dwindled with the disappearance of that process industrially, but it is still available in a pure form at a reasonable price – which is not true of the costly and uncertain iron(III) oxalate, and which is not listed in the fine chemicals database. For all the reasons given above, the preferred choice of iron(III) compound for noble metal sensitizers is obvious.

IV.3 Problems of Chrysotype Chemistry

The chief difficulty in applying the iron-based system to printing in gold arises from the strongly oxidising nature of the most commonly available gold compounds, salts of the tetrachloroaurate(III) anion, for which the redox potential is:

$$E^o([AuCl_4]^-/Au,4Cl^-) = +1.00\ V$$

This redox potential is high enough to cause oxidation of the carboxylate anion, citrate or oxalate, which would be present in the mixed sensitizer, with consequent premature deposition of gold metal, *e.g.* for oxalate the equation is:

$$2[AuCl_4]^- + 3C_2O_4^{2-} \rightarrow 2Au + 6CO_2 + 8Cl^-$$

tetrachloroaurate anions + oxalate anions → gold metal + carbon dioxide + chloride anions

Herschel partially solved this problem by using the gold(III) salt, sodium tetrachloroaurate(III), as a separate development bath for an exposed coating of ammonium iron(III) citrate, but this is now a very costly and wasteful way to proceed, because the gold solution is immediately contaminated by the excess iron salts and cannot be reused. Simply brushing on the developer, in

an attempt at economy, leads to uneven results. An additional disadvantage of using tetrachloroaurate(III) arises from the 1 : 3 stoicheiometry of the reduction:

$$Au(III) + 3Fe(II) \rightarrow Au(0) + 3Fe(III)$$

gold(III) + iron(II) → gold metal + iron(III)

which lowers the quantum yield of gold metal in the final image by a factor of three, leading to lower optical densities. Again, this is a simplified version of the chemistry; the actual molecules involved are complex:

$$[AuCl_4]^- + 3[Fe(C_2O_4)_2]^{2-} \rightarrow Au + 3[Fe(C_2O_4)_2]^- + 4Cl^-$$

tetrachloroaurate(III) + bisoxalatoferrate(II) → gold + bisoxalatoferrrate(III) + chloride

The Au(III) is a vigorous oxidising agent, which causes an unacceptably high contrast in the gold images made by this chemistry.

IV.4 Chemistry of New Chrysotype: Gold(I) Complexes

Clearly the solution to these problems lies in finding a suitable compound, preferably of gold(I), having a diminished redox potential with respect to the metal so that it can tolerate the presence of oxalate. Most simple binary compounds of gold(I) in an aqueous environment are unstable with respect to disproportionation into the metal and gold(III):

$$3Au(I) \rightarrow 2Au(0) + Au(III)$$

so it is necessary to seek the answer among the complexes of gold(I). Until fairly recently, the only well-known water-soluble, stable gold(I) complexes were, typically, the sulphito, cyano, thiocyanato, and thiosulphato species, $[Au(SO_3)_2]^{3-}$, $[Au(CN)_2]^-$, $[Au(SCN)_2]^-$ and $[Au(S_2O_3)_2]^{3-}$, respectively. But these complexes have such large formation constants that the redox potential is depressed to values below even that of the iron photoproduct, e.g.:

$$E^o([Au(CN)_2]^-/Au,2CN^-) = -0.6\ V$$

so they cannot be reduced to gold metal by iron(II).
The first objective of this work was therefore to find a soluble gold(I) complex of intermediate stability: to this end, many potential ligands were tested by reacting them with tetrachloroaurate(III), then mixing the product with ammonium trisoxalatoferrate(III) solution to see if a suitable sensitizer resulted.[65] The criteria for suitability were:

- The ligand should form a gold(I) complex that is thermally stable in aqueous solution, but reducible to the metal by the iron(II) photoproduct.
- The ligand should not cause precipitation of an insoluble gold complex at the high concentrations (ca. 0.3 M) needed to give adequate coating weight when imbibed into paper.
- The ligand should not react significantly with the trisoxalatoferrate(III) anion.
- The ligand should not be malodorous or highly toxic.
- The mixed sensitizer should be stable for at least ten minutes under ambient conditions, to allow coating of paper without perceptible precipitation of gold.

- Exposure to UVA (365 nm) light of the sensitized paper in contact with a step tablet should yield a well-graduated print of long tonal scale, smooth texture, high D_{max} and no chemical fog after appropriate wet processing (see below).

The history of the investigation of several ligands is summarized in my book, *Gold in Photography*. Ultimately, a ligand satisfying all these criteria was found: viz., 3,3'-thiodipropanoic acid, $S(CH_2CH_2COOH)_2$, used in the form of its disodium or diammonium salts, which are highly soluble in water. The reaction of this ligand with tetrachloroaurate(III) follows a path already well-established for other thioethers by Cattalini and co-workers.[66,67] The generality of this reaction has also enabled McAuliffe and colleagues[68] to devise a synthesis for neutral gold(I) complexes that are water insoluble and therefore readily isolated and characterised.[69] From kinetic studies[70] it is found that the reaction mechanism takes place in two steps, as follows (for brevity the ligand formula will be written as SR_2):

(1) Coordination of the ligand with tetrachloroaurate(III), displacing chloride:

$$[AuCl_4]^- + SR_2 \rightarrow [AuCl_3SR_2] + Cl^-$$

(2) Attack of a second molecule of ligand on the gold(III) complex, reducing it to a two-coordinate gold(I) complex, the thioether ligand being itself oxidised in the presence of water to the corresponding sulphoxide:

$$[AuCl_3SR_2] + SR_2 + H_2O \rightarrow [AuClSR_2] + OSR_2 + 2H^+ + 2Cl^-$$

It is believed that this reductive step may take place via transfer of a chlorine atom from gold to sulphur, followed by hydrolysis.

(3) In the presence of excess ligand, an equilibrium is also possible, in which a third molecule of the ligand may displace the chloride ion from the gold(I) complex:

$$[AuClSR_2] + SR_2 = [Au(SR_2)_2]^+ + Cl^-$$

These equations illustrate the reaction steps in a formalised manner only; the precise species present, and the states of ionization of the carboxylate functions at equilibrium, will obviously depend on the cation, pH, and metal/ligand ratio. The speciation in this system is complex, and its investigation is hindered by the fact, apparent from the ^{13}C nmr spectrum, that the equilibria for ligand exchange at gold(I) are labile and rapid.[71]

IV.5 Warning: Fulminating Gold

Whenever ammonia is added to gold(III) compounds, the dangerously sensitive explosive, fulminating gold, will usually be precipitated.[72] This substance is mentioned here for one very good reason only: in any experimental work with gold, its formation must be scrupulously ***avoided***. But rather than leave the reader in ignorance of this danger, the author takes the view that a hazard known and understood, is a hazard that can be negated. Fulminating gold is formed whenever a gold(III) compound is mixed with ammonia, or ammonium hydroxide, or ammonium carbonate, or any *alkaline* ammonium salt[73] – all of which have been excluded from the chemicals used in this work. It is a brownish-yellow or olive-green insoluble powder, which is highly shock-sensitive. When dry, it detonates with

extreme violence by friction or heat, or sometimes even with the lightest touch. It enjoys the distinction of being one of the most sensitive explosives known to man – and it must offer one of the most expensive means of mutilating oneself! It was a favorite substance with the more flamboyant alchemists, and the 12-year-old Henry Fox Talbot was nearly expelled from Harrow School for causing an alarming explosion with this substance, while trying to gild steel.

IV.6 The Chemical Nature of Paper[74]

The paper substrate is a chemically reactive component of the process and deserves close consideration, so that we can understand its influence on the image. Paper consists primarily of an interlocked web of the fibrous natural product, cellulose, which is the chief constituent of all plant tissues. Cellulose is a polymeric 'carbohydrate', with empirical formula approximately CH_2O, but is more precisely described chemically as a polysaccharide, a linear (ß-1,4 linked) polymer of the sugar, β-D-glucopyranose ($C_6H_{12}O_6$),[75] each molecule of which loses a water molecule (H_2O) in the process of forming an ether linkage (-C-O-C-) to the next, so the formula of cellulose is $(C_6H_{10}O_5)_n$ the polymer containing ca. n = 15,000 of these monomer units in the strong, long-chain form of cellulose, known as α-cellulose.[76] (figure AIV.1)

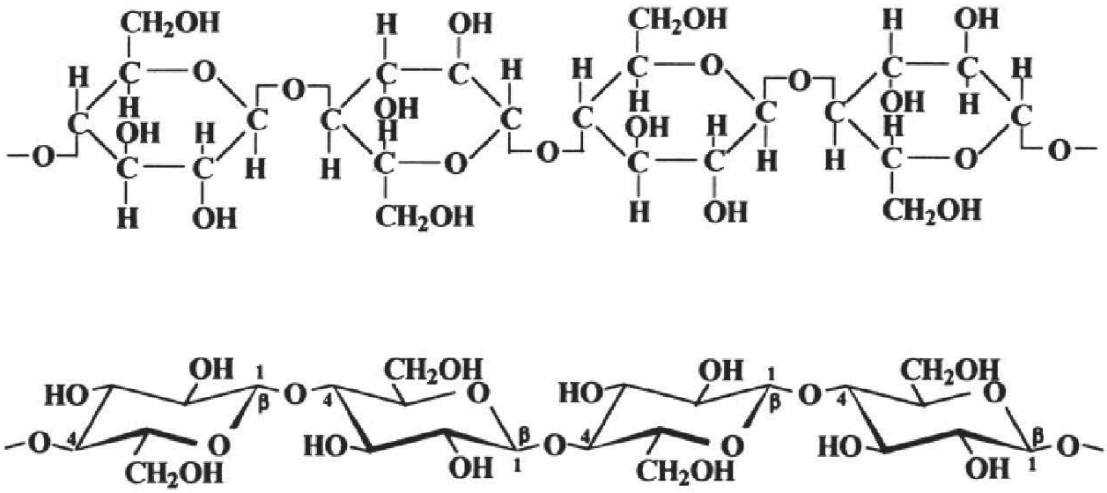


Figure AIV.1 Alpha-cellulose structure.

Cellulose is vulnerable to acids, which split the ether linkages, restoring the lost water molecules as hydroxyl groups (-C-OH HO-C-), and thus cause scission of the chains, and embrittlement of the paper sheet.

The individual cellulose molecules cohere into bundles called microfibrils, each containing about 100 parallel molecular chains, held together largely by the attraction of their polar hydroxyl groups, that the chemist calls 'hydrogen-bonding'. The structure is partly crystalline, partly amorphous. There is an ascending scale of fibrous structure in cellulose: the microfibrils, of dimensions ca. 10 x 3.5 nm in cross section and ca. 1000 nm (1 µm) long, which can only be seen with an electron microscope, cohere

into fibrils, ca. 0.5 μm thick and 100 μm long, which comprise the cell walls and are visible in a light microscope; these in turn bundle together to form the visible plant fibre or 'hair', ca. 40 μm thick and 1 cm or more long.

The description so far has ignored any chemical role played by the cellulose paper substrate. It is likely that the components of the sensitizer will be wholly or partially chemisorbed onto the cellulose, especially those with a propensity for hydrogen-bond formation, such as $[Fe(C_2O_4)_3]^{3-}$ or aquated derivatives thereof, like $[Fe(C_2O_4)_2(H_2O)_2]^-$. Cellulose itself naturally absorbs water from a normal humid atmosphere to a degree that is well-documented, but the concentration of water in the paper fibres will also depend on the other chemicals present in the sensitizer, especially on the cations used for the complex salts of iron and the noble metal, which may confer hygroscopic or deliquescent properties on the sensitizer. If the sensitized paper is not completely heat-dried, but allowed to equilibrate at ambient RH, then it will also contain significant amounts of absorbed water, as indicated by the cellulose/water absorption curve (figure AIV.2).

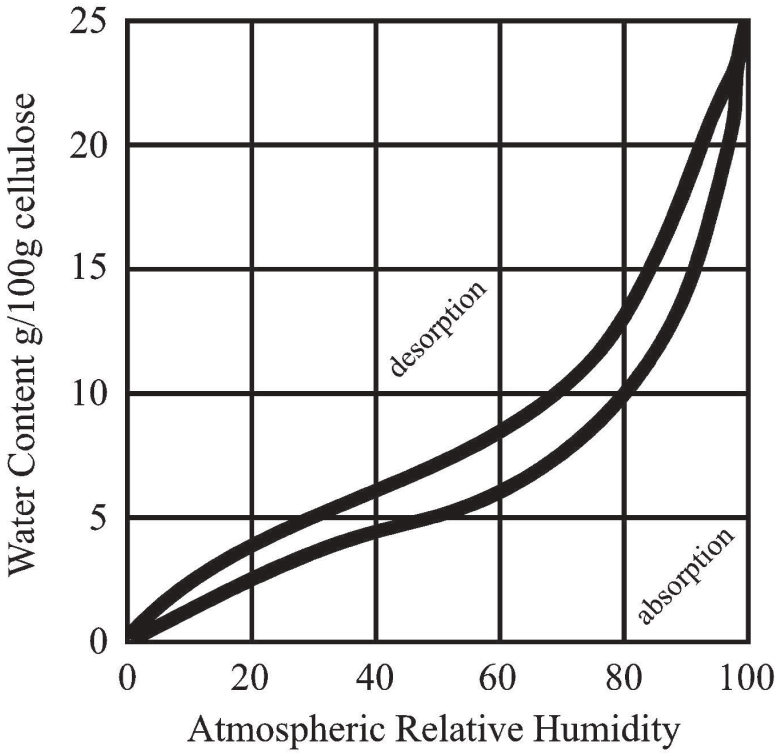


Figure AIV.2. Cellullose/water absorption curve.

There are three distinct regions to this curve, as the humidity increases: initially there is a small but sharp rise corresponding to the 'bound' water that is chemisorbed strongly onto the cellulose; this is followed by a long, gradual, and nearly linear uptake corresponding to the 'interfibrillar' water; finally there is a steep rise, without obvious limit, when the paper 'imbibes' copious amounts of water into its capillaries at RH values approaching 100%. Recalling the microporous structure of cellulose fibres described above; under conditions of high relative humidity, we can calculate that there is sufficient water hydrogen-bonded within the amorphous regions of the cellulose structure (about ten molecules of water locally to each one of

trisoxalatoferrate(III)) to confer a limited mobility on the sensitizer ions in the interfibrillar space and allow reaction to take place within the apparently 'dry' paper.

IV.7 The Importance of Humidity

The formation of a permanent image by the iron-based photographic printing processes takes place, as we have seen, in two stages of chemical reaction: first is the photochemical step, in which the UV light transforms the iron(III) carboxylate (citrate, oxalate, tartrate, etc) in the sensitizer into an iron(II) carboxylate. The visible effect of this is slight; only the shadow tones of the image become apparent, and at most the colour may change from pale green to pale yellow, or pale yellow to pale brown. The iron(II) photoproduct is not stable indefinitely, either, and the second stage of transforming it into a permanent image must follow fairly promptly if the pale image is not to be re-oxidised by air back to iron(III) and therefore lost. The second step – a redox (*red* uction-*ox* idation) reaction – is the formation of the final image in precious metal by the reaction between the iron(II) photoproduct and the noble metal compound incorporated in the sensitizer – usually a compound of platinum, palladium, silver, or gold. The reaction between these two cannot occur in totally dry paper, however, because the chemicals are static, either as separate crystals in the solid state, or possibly chemically adsorbed onto the cellulose fibres. The presence of some water is necessary, as described above, to dissolve and locally mobilise the iron(II) and noble metal salts (provided they are soluble), and to help them diffuse the short distances needed for contact with one-another within the fibres, when the reaction to form the metal image can occur. To provide this water, there are two main options:

1. to use an aqueous processing bath to 'develop' the image *after* the exposure
2. to ensure that sufficient moisture is present in the paper fibres in the first place, to enable 'print-out' *during* the exposure.

The meaning of 'development' here is rather different from the significance that it carries in conventional silver-gelatin processing. There is no amplification of the effects of the light, and no binder is present, the reaction occurs in solution, not to a latent image in the solid halide.

The traditional iron-based processes employing iron(III) oxalate must be wet-developed, because the photoproduct from this salt is highly insoluble, iron(II) oxalate:

$$h\nu + Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4\,(s) + 2CO_2$$

which needs a strong solution of oxalate ions, or other complexing agent, to solubilise it for reaction:

$$FeC_2O_4 + C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_2]^{2-}$$

In contrast, the print-out processes employ a salt of the ferrioxalate anion (e.g. ammonium iron(III) oxalate). The photoproduct in this case is an iron(II) oxalato-complex:

$$h\nu + 2[Fe(C_2O_4)_3]^{3-} \rightarrow 2[Fe(C_2O_4)_2]^{2-} + 2CO_2 + C_2O_4^{2-}$$

which is soluble and reactive enough to reduce the noble metal salt directly, without a 'developer' solution, provided that there is sufficient water present. Many printers find this a more satisfactory way to proceed, because it confers all the benefits of a print-out image, which will be considered below.

It should be realised that, in order to provide sufficient water molecules within the fibres of the paper sheet for this short-range diffusion of ions to occur, the paper does not have to be wet, or even perceptibly damp. As described above, paper that has been conditioned in an environment with a moisture content of ca. 70% RH at 20° C, for instance, will contain an amount of water in its fibres ca. 8% by weight, which is quite sufficient to facilitate the image-forming redox reaction, yet the sheet still 'rattles' and is, to all appearances, dry. This figure for the water content may be modified by the presence in the sensitized layer of any hygroscopic or deliquescent substances.

The benefit of allowing the image to form by print-out is that no chemicals are lost from the paper at this important stage, and a very complete and permanent printed-out image can be obtained. On the other hand, as soon as an exposed plain-paper sensitizer is immersed in a wet-processing bath – a water solution intended to 'develop' the image and 'clear' the excess chemicals – then the soluble constituents of the exposed sensitizer begin to leach out of the paper fibres into the bulk of the processing solution, where they are diluted and lost for imaging purposes. If the reaction between the photochemicals to form the image substance takes place as slowly as this washing-out of them, then the image will obviously be weak and incomplete. This is the besetting problem of the traditional platinotype process, where the chemistry of the redox reaction is intrinsically slow, and requires a developing agent to solubilise the iron(II) oxalate photoproduct; however, as soon as the print is immersed in an aqueous developer bath, the image-forming chemicals begin to dissolve out before they can fully react, leaving a weak and fibrous or grainy image.

Unreacted chemicals extracted into the wet development bath may also flow back into the paper and cause problems by reacting elsewhere to stain the high values, or 'bleed' at the edges of regions of high density. For a good quality of image, making the fullest use of the chemistry of the sensitizer, it is essential to ensure that there is sufficient water in the paper fibres either *before* or *after* exposure. This may be simply introduced from the vapour by hydrating the paper sheet in an atmosphere of controlled relative humidity.

If hydration is performed *before* exposure, then a substantial degree of print-out results, with several attendant advantages and characteristics:

- correct exposure can be found by inspection,
- the process is self-masking and so accommodates a wide range of exposure without 'blocking up' the shadow tones,
- negative contrast does not have to be controlled too precisely, because dense highlights can be 'printed down', accommodating a range of contrast in the negative which enables very delicate gradation in the high values,

- there is no need to impose a strict method of contrast control on the composition of the sensitizer, which is often deleterious to the image quality; for instance, the addition of potassium chlorate or dichromate to the platino-palladiotype can cause graining and truncation of the tonal scale.

If vapour hydration is performed *after* exposure (but before wet-bath processing) and if the chemistry is sufficiently reactive, the image develops as the water vapour is absorbed, with the advantages of little diffusion, no loss or staining of the image, and smooth tones. The process may be continuously inspected, and the print withdrawn when it has gone far enough. This is also what occurs in the 'breath-developed' processes.

The quantity of water present in the cellulose fibres will also have an important governing effect on the particle size of the image substance, which is a colloidal metal, and hence on the colour of the image. A large reservoir of capillary water will permit greater amounts of substances to react locally and therefore make it possible for the particles of metal to grow larger. Such particles will appear more neutral in hue. A very restricted pool of capillary water will constrain the chemistry to producing small metal particles only, which can show quite marked colours – brown or sepia for silver and palladium, and even pink, magenta and blue in the case of gold. Thus, regulating the hydration of the paper controls the colour of the image.

IV.8 The Chemistry of Print Clearing

Once the noble metal image has been fully formed within the paper fibres, it only remains to remove completely the excess chemicals – sensitizer and reaction products – to reach a stable image. The process of development and clearing described in this manual has been evolved over the years, and is intended to achieve this most thoroughly and expeditiously. Lest it should be thought that the choices for this procedure are arbitrary, their logic will be explained here.

The exposed and printed-out sensitizer layer will contain, in addition to the nanoparticle gold (or other noble metal) image: ions of iron(III) complexes, oxalate, chloride, the gold(I) complexes of thiodipropanoic acid, and residual developing agent (tartrate, citrate etc.). Most of these are soluble in water and will be easily removed in the washing. The chief problem of effective clearing is the iron(III): at any pH above 4, this tends to hydrolyse, forming polymeric colloidal iron(III) hydroxide, which can lodge in the paper fibres imparting a yellow stain. Moreover any calcium ions in the washing water ('hardness') will tend to precipitate insoluble calcium oxalate, and promote hydration and hydrolysis of the Fe(III) complex:

$$Ca^{2+} + [Fe(C_2O_4)_3]^{3-} + 2H_2O \rightarrow CaC_2O_4\ (s) + [Fe(C_2O_4)_2(H_2O)_2]^-$$

$$\rightarrow \text{etc} \rightarrow [Fe(H_2O)_6]^{3+} \rightarrow \text{etc} \rightarrow Fe(OH)_3\ (s) \rightarrow FeO(OH)\ (s)$$

While freshly-formed iron(III) hydroxide can be dissolved in dilute acids initially, if it is not soon removed it slowly (over a period of days) transforms irreversibly into a highly insoluble polymeric form of iron(III) oxide-hydroxide, FeO(OH) – a mineral called Goethite – which is quite insoluble in dilute acids. It is therefore essential to remove all the iron(III) at the

processing stage before the print dries, and this is achieved with the following sequence:

1. An acidic first bath, preferably disodium EDTA, which at pH 4, avoids hydrolysis, and chelates iron(III) well.
2. A sulphite or metabisulphite, Na_2SO_3 or $Na_2S_2O_5$, which reduces the residual iron(III) to iron(II), which is more easily removed:

$$2Fe^{3+} + SO_3^{2-} + H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 2H^+$$

3. Tetrasodium EDTA, which at pH 9, chelates residual iron(II) well, removing the last traces of iron and leaving the paper in an alkaline condition, desirable for its preservation.

It is important not to use tetrasodium or trisodium EDTA for the first processing bath – both have a high pH (9 and 7 respectively) at which the iron (III) is not effectively complexed, but rather hydrolysed and yellow or brown staining will result. The Na_4EDTA bath, after the sulphite lasts much longer, because there is so little iron left in the prints by the time they reach it; most comes out in the first bath.

IV.9 Removal of Iron Stains

In the event that an iron-based print, such as platinotype or chrysotype, for whatever reason, does develop yellow stains of residual iron, they may be removed, or at least markedly diminished, by the following procedure which has been investigated by Gent and Rees.[77]
The print is immersed in a bath of 5% tetrasodium EDTA and 5% sodium dithionite, $Na_2S_2O_4$; the pH of this bath is about 8.5. The period of immersion may have to be quite lengthy – an hour or two – and the print should then be re-washed. The dithionite is a very powerful reducing agent which attacks the FeO(OH), reducing it to iron(II), which is then chelated by the EDTA. The bath does not keep, and should be made up fresh.

Table A4.1 Table of %RH Values equivalent to those at 20°C (in absolute water content [H_2O] mg/litre)

%RH at 20°C		100	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5
[H_2O] mg/l		17.30	16.44	15.57	14.71	13.84	12.98	12.11	11.25	10.38	9.52	8.65	7.79	6.92	6.06	5.19	4.33	3.46	2.60	1.73	0.87
T °C																					
10	9.40											92	83	74	64	55	46	37	28	18	9
11	10.01										95	86	78	69	60	52	43	35	26	17	9
12	10.66									97	89	81	73	65	57	49	41	32	24	16	8
13	11.35								99	91	84	76	69	61	53	46	38	30	23	15	8
14	12.07							100	93	86	79	72	64	57	50	43	36	29	21	14	7
15	12.83							94	88	81	74	67	61	54	47	40	34	27	20	13	7
16	13.63						95	89	83	76	70	63	57	51	44	38	32	25	19	13	6
17	14.84				99	93	87	82	76	70	64	58	52	47	41	35	29	23	17	12	6
18	15.37				96	90	84	79	73	68	62	56	51	45	39	34	28	23	17	11	6
19	16.21			96	91	85	80	75	69	64	59	53	48	43	37	32	27	21	16	11	5
20	17.30	100	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5
21	18.34	94	90	85	80	75	71	66	61	57	52	47	42	38	33	28	24	19	14	9	5
22	19.43	89	85	80	76	71	67	62	58	53	49	45	40	36	31	27	22	18	13	9	4
23	20.58	84	80	76	71	67	63	59	55	50	46	42	38	34	29	25	21	17	13	8	4
24	21.78	79	75	71	68	64	60	56	52	48	44	40	36	32	28	24	20	16	12	8	4
25	23.05	75	71	68	64	60	56	53	49	45	41	38	34	30	26	23	19	15	11	8	4
26	24.38	71	67	64	60	57	53	50	46	43	39	35	32	28	25	21	18	14	11	7	4
27	25.78	67	64	60	57	54	50	47	44	40	37	34	30	27	23	20	17	13	10	7	3
28	27.24	64	60	57	54	51	48	44	41	38	35	32	29	25	22	19	16	13	10	6	3
29	28.78	60	57	54	51	48	45	42	39	36	33	30	27	24	21	18	15	12	9	6	3
30	30.38	57	54	51	48	46	43	40	37	34	31	28	26	23	20	17	14	11	9	6	3
31	32.07	54	51	49	46	43	40	38	35	32	30	27	24	22	19	16	13	11	8	5	3
32	33.83	51	49	46	43	41	38	36	33	31	28	26	23	20	18	15	13	10	8	5	3
33	35.68	48	46	44	41	39	36	34	32	29	27	24	22	19	17	15	12	10	7	5	2
34	37.61	46	44	41	39	37	34	32	30	28	25	23	21	18	16	14	11	9	7	5	2
35	39.63	44	41	39	37	35	33	31	28	26	24	22	20	17	15	13	11	9	7	4	2
36	41.75	41	39	37	35	33	31	29	27	25	23	21	19	17	15	12	10	8	6	4	2

Appendix V Quantitative Photochemistry

V.1 Basic Laws of Photochemistry

In summarising the principles of photochemistry there are five basic 'Laws' relating to photochemical processes; none is rigorously true, but all are sufficiently valid to be useful for understanding the behaviour and for making approximate calculations:

V.1.1 The Grotthuss-Draper Law

Photochemical theory had its beginnings with the Grotthuss-Draper Law (ca. 1818), which is a commonsense statement that, for light to have any effect on matter, it must first be absorbed:

Only the light absorbed by a substance may induce a chemical change within it.

Light is a form of energy. Across the visible spectrum, going from red to blue, the intrinsic energy of the light nearly doubles (see Planck's Law below). When a molecule absorbs a photon of light (visible or UV), its internal energy is increased, and it is said to be lifted into an 'excited' state. Sooner or later, this excitation energy is transformed and lost, so that the molecule returns to its normal or 'ground' state. This process is appropriately called 'relaxation'. The manner of the transformation of the absorbed energy, however, can be various, and it depends on the lifetime of the excited state and other factors. The least interesting, and most common process is 'thermal relaxation', that is the dissipation of the excess energy as heat which is manifested as more agitated motion of the molecules. More interestingly, in some spectacular cases, part of the excess energy may be re-emitted as light, giving us the attractive and useful luminescent phenomena, which are called fluorescence and phosphorescence, depending on whether the excited state is short- or long-lived, respectively. Most importantly for our purposes, the excess energy may bring about a chemical reaction if the molecular circumstances are favourable. It should come as no surprise that a molecule in an excited state is capable of more vigorous chemical reactions than when in its ground state. Ultra-violet light is often required to supply sufficient energy for such chemical transformations.

V.1.2 The Stark-Einstein Law

There is an equivalence between the quantity of light absorbed and the amount of substance that is chemically transformed, both of which are measurable, and may be related by an elementary principle of quantum theory, as it applies to photochemical changes.[78] This principle dates from *ca* 1912 and is usually referred to as the Stark-Einstein Law. It is easily appreciated without invoking much jargon, and the non-technical reader should readily see that it amounts to nothing more than a statement of 'good book-keeping' at the molecular level. The Stark-Einstein Law effectively requires that:

For each molecule of substance to be transformed, one photon must be absorbed.

(A photon is the fundamental, indivisible particle or 'quantum' of light.) The extent to which this 'Law' is obeyed may be quantified by defining the quantum yield as:

ϕ = number of molecules reacted / number of photons absorbed

The units of ϕ are moles/einstein.

When ϕ = 1.000, the Stark-Einstein Law is obeyed exactly. Apparent departures from ϕ = 1, significantly greater than one, arise when the primary light reaction triggers secondary reactions; this is the case in iron-oxalate photochemistry, where one photon leads to the reduction of two ions of Fe(III) as may be seen in the equations above: here ideally ϕ = 2. The quantum yield can quite commonly appear to be less than ideal, however, due to competing reactions or processes which diminish the efficiency of the photochemical process.

V.1.3 Planck's Law

There is equivalence between the energy, *E*, of a photon and the frequency ν of the radiation, as given by the quantum theory of Max Planck (1900):
The energy of a photon is directly proportional to its frequency:

$$E = h\nu$$

The constant of proportionality is Planck's constant:

$$h = 6.626 \times 10^{-34} \text{ Joule seconds}$$

The frequency, ν, and wavelength, λ, of electromagnetic radiation are related by the speed of light, *c* :

$$\nu\lambda = c = 2.998 \times 10^{8} \text{ metres/second}$$

V.1.4 The Bunsen-Roscoe Law

In photochemical exposures, intensity and time are reciprocal.
This is enshrined in the definition of light exposure, *H*, as equal to the intensity of the light, *I*, multiplied by the time of duration, *t*, of the exposure:

$$H = It$$

Thus, for a given exposure, the intensity is proportional to the reciprocal of the time, and *vice versa*. This relation only has a limited range of validity, for a variety of reasons: for very high or very low light intensities, the exposure times required to produce the same effect as that of average light intensity are longer than the definition would predict. This non-compliance is called 'reciprocity failure' and is a property of camera film familiar to any practising photographer.

V.1.5 The Beer-Lambert Law

Refers to the absorption of light passing through a homogeneous medium;
The optical density, *D*, is directly proportional to the molar concentration, *C*, and the path length, *d*:

$$D = \varepsilon Cd$$

The constant of proportionality, the molar extinction coefficient, ε , is also called the *molar absorptivity* for a given substance, and conventionally has (non-SI) units of $dm^3\ mol^{-1}\ cm^{-1}$.
In terms of the intensities of light, incident I_o and transmitted I_t , by the sample, it may be shown that:

$$\log_{10}(I_o/I_t) = D \quad \text{or} \quad I_t/I_o = 10^{-D}$$

V.2 Effect of Excitation Wavelength on Photochemical Yield

There are four main factors influencing the wavelength dependence of the yield of an alternative photographic printing process:

V.2.1 The spectral power distribution of the light source.

The energy emitted by a light source varies with the wavelength in a manner that can be plotted, for instance, a lamp of Phillips type /05 emits a spectrum of light energy as shown (figure A5.1).

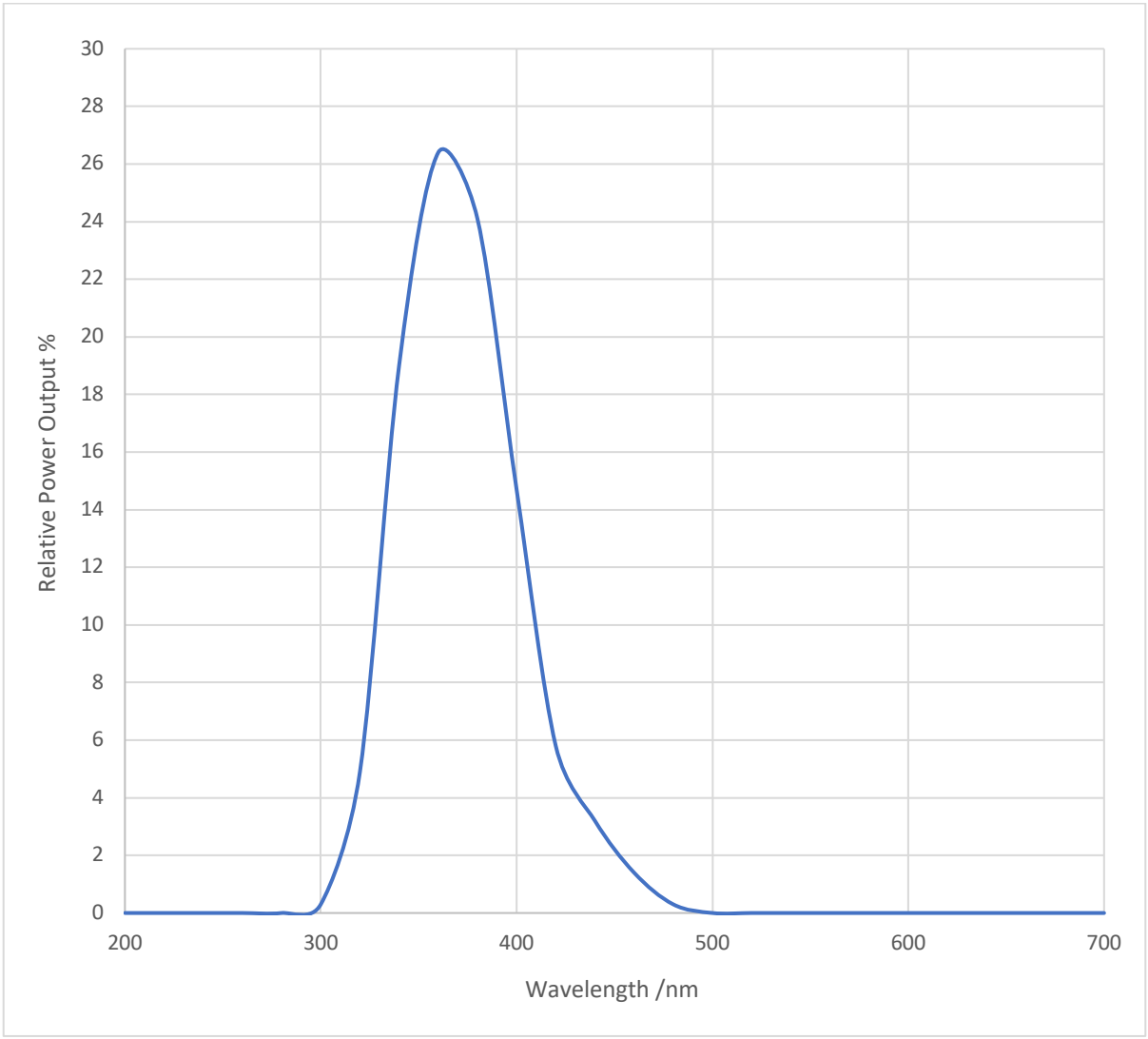


Fig. A5.1 Relative output of Phillips Actinic/05 UV lamp

It is the area under this curve, between appropriate wavelength limits, that determines the yield, not just the height of the peaks in the emissivity. The spectral power per unit bandwidth must be integrated over the wavelength range. In practice this can be done by taking thin slices of the spectrum every 10 or 20 nm, calculating the effect at each sample wavelength, and summing the results over the whole wavelength range. More simply, the approximate proportions of lamp output at various wavelengths are tabulated as follows:

Table A5.1. Relative emissivity of actinic /05 UV lamp at wavelength

Wavelength	300	320	340	360	380	400	420	440	460	480 nm
Rel. Output	0.3	4.9	19.0	26.4	24.1	14.7	5.8	3.2	1.4	0.3 %

V.2.2 The variation of quantum yield with wavelength.

The intrinsic response is expressed by the quantum efficiency or quantum yield of the primary photochemical process.[79] The quantum yield, ϕ, for the photolysis of the trisoxalatoferrate(III) ion in aqueous solution has been determined reliably at several wavelengths of the mercury emission spectrum by a number of independent workers.[80] All agree that a value of ϕ slightly greater than unity obtains over the wavelength range from 250 to 450 nm, but begins to fall off sharply above 500 nm, becoming insignificant in the green/yellow regions of the spectrum and beyond, as shown below.[81]

Table A5.2. Quantum yield ϕ (per mole of iron) for the ferrioxalate anion determined at various wavelengths λ (Mercury lines)

λ	254	313	365	405	436	468	509	546	579	620	nm
ϕ	1.25	1.24	1.18	1.14	1.05	0.93	0.86	0.15	0.01	0.01	

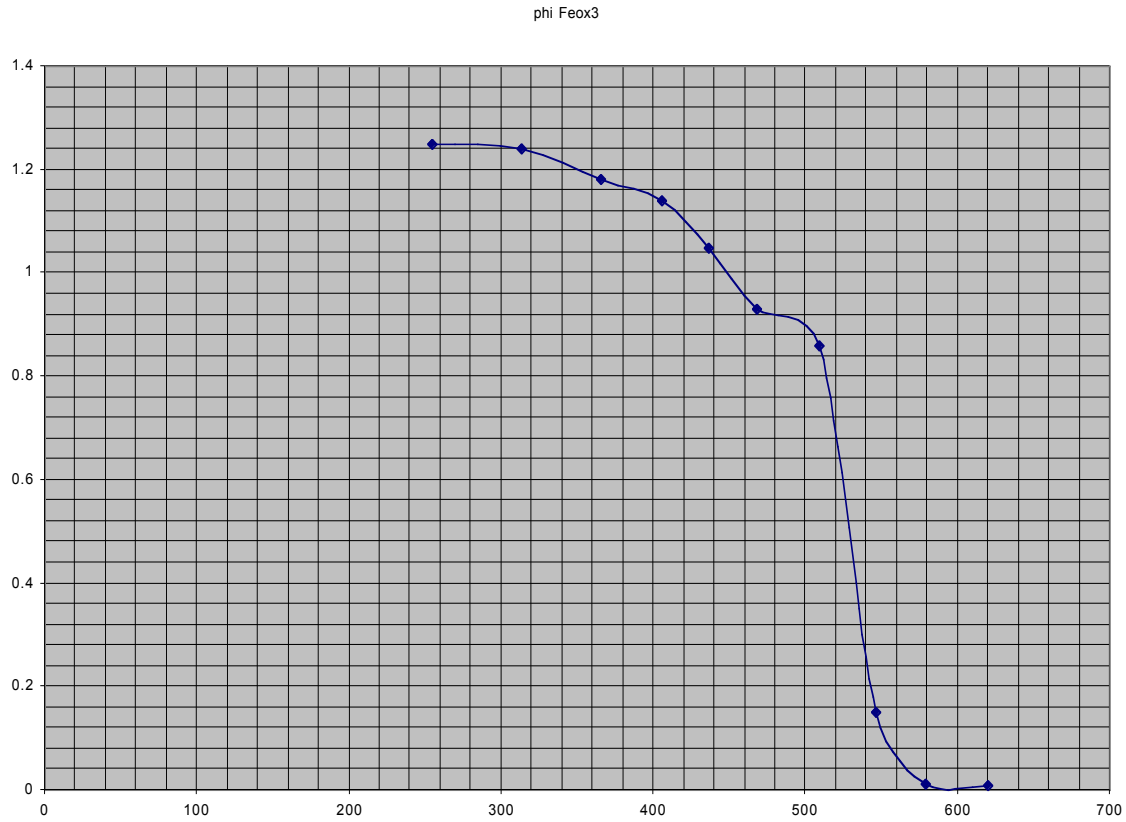


Figure A5.2. Quantum yields for the photolysis of aqueous $[Fe(C_2O_4)_3]^{3-}$

In contrast with the data measured for the aqueous solution, the determination of ϕ for trisoxalatoferrate(III) in the solid state is beset with difficulties arising from geometrical-optical effects and the physical state of the sample. Values of ϕ ranging from 0.15 to 1.3 at 365 nm have been reported[82] and the origins of these seemingly discordant results have been discussed in some depth; a value of $\phi = 0.68$ at 365 nm seems most reliable.[83] It is also significant that ϕ has been found to be sensitive to the presence of oxygen;[84] it is therefore important that the exposing paper should not have uneven access to the atmosphere when in its printing frame. We see that between 300 and 500 nm the quantum efficiency does not vary very much, and it is the least important factor in determining the variation of yield with wavelength.

V.2.3 Fraction of incident light absorbed by the photoactive species.

This is determined partly by the absorption spectrum of the trisoxalatoferrate (figure A5.3) but it must also take account of any 'internal filter effect': many alternative process sensitive coatings also contain coloured substances that do not contribute significantly to the light-sensitivity (i.e., the pigment in gum bichromate and carbon; the potassium ferricyanide in cyanotype; the noble metal salts in platino-palladiotype). These substances absorb the printing light as it passes through the coating, and give nothing in return (on the assumption that there is no energy transfer). The presence of these coloured (and UV-absorbing) substances is like the effect of a coloured filter over the light source - except that the filter is 'built-in', and inescapable.[85] This is called the 'internal filter effect' and it may be quantified using the Beer-Lambert Law.

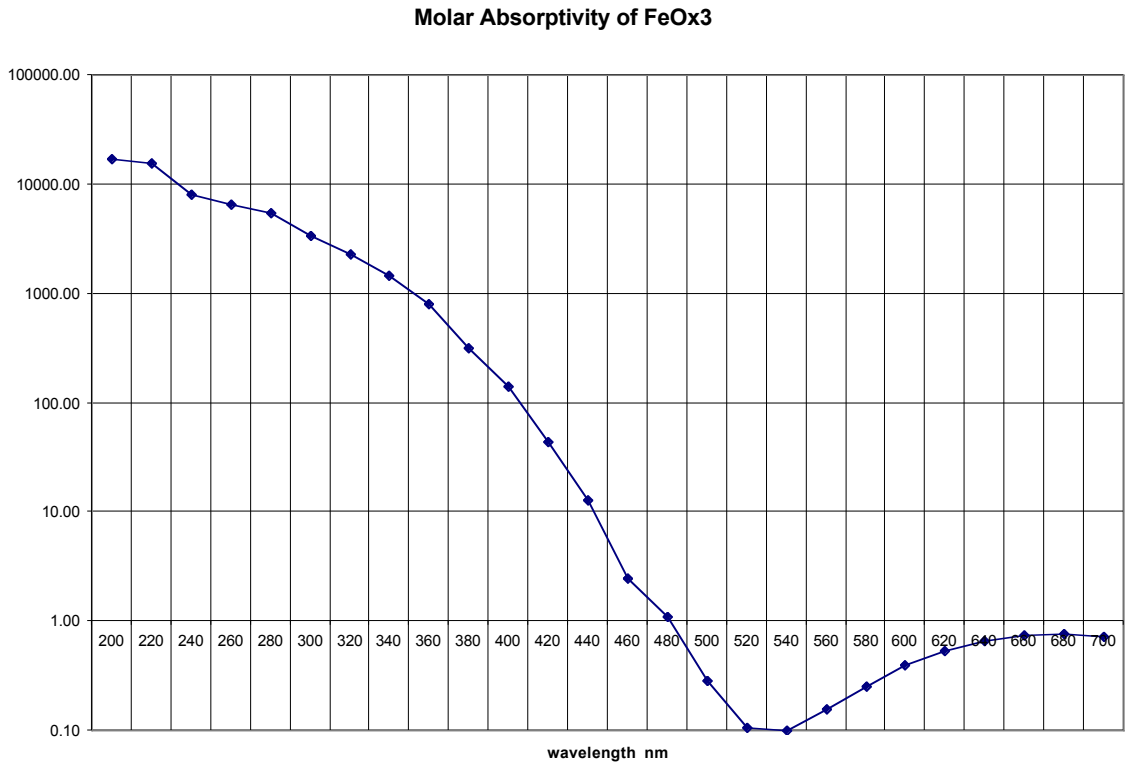


Figure A5.3. The UV-visible absorption spectrum of $[Fe(C_2O_4)_3]^{3-}$

For a two-component system, in which ε_{Fe} and C_{Fe} denote the molar absorptivity and concentration of the photoactive component, trisoxalatoferrate(III), and ε_M and C_M denote the same parameters for the inert filter substance, the metal salt, the total optical density D of the layer, assuming the Beer-Lambert law holds,[86] is:

$$D = (\varepsilon_{Fe}C_{Fe} + \varepsilon_M C_M)d$$

where d is the layer thickness in cm. The concentration C_M of the metal salt is related to C_{Fe} the concentration of the trisoxalatoferrate(III), in the sensitizers used here, by the stoicheiometry of the redox reaction:

$$\text{Fe:Ag} = 1{:}1;\ \text{Fe:Au(I)} = 1{:}1;\ C_M = C_{Fe}$$

$$\text{Fe:Pt(II)} = 2{:}1;\ \ \text{Fe:Pd(II)} = 2{:}1;\ C_M = 0.5C_{Fe}$$

The fraction of incident light absorbed in total by the layer of sensitizer is then given by the Beer-Lambert Law:

$$(I_o - I_t)/\ I_o = 1-10^{-D}$$

but the fraction of incident light absorbed by the photoactive component *only* in the sensitized layer is a proportion of this given by:

$$f = (1-10^{-D})\ \varepsilon_{Fe}C_{Fe}d\ /D$$

f is strongly wavelength-dependent due to the steeply falling extinction coefficient of the trisoxalatoferrate(III) absorption spectrum with wavelength. In those sensitized layers where the metal salt has an intense absorption spectrum, there is additionally the 'internal filter' effect. Knowing the absorption spectra (in terms of their molar extinction coefficients) of the two components, trisoxalatoferrate and metal salt, and the molar coating weight W of the sensitizer,

The molar coating weight, W, of photosensitive iron complex is given by the molarity of the iron in the coating solution ([Fe] = 0.7 M for Pt-Pd sensitizers, but ca. 0.16 M for the gold sensitizers used here) multiplied by its specific coating volume in units of $dm^3\ m^{-2}$ (0.024 for a typical sized paper, see Chapter 2 p 30), so:

$$W = 0.7 \times 0.024 = 0.0168 \text{ mol m}^{-2} \text{ for Pt-Pd}$$

$$W = 0.16 \times 0.024 = 0.00384 \text{ mol m}^{-2} \text{ for Au}$$

The concentration C_{Fe} in mol dm^{-3} multiplied by the effective optical path length, d, in cm is related to the coating weight, W, by:

$$C_{Fe}d = 0.1W = 0.00168 \text{ cm mol dm}^{-3} \text{ for Pt-Pd}$$

$$C_{Fe}d = 0.1W = 0.000384 \text{ cm mol dm}^{-3} \text{ for Au}$$

The factor of 0.1 is included to take account of the units (cm) customarily used for d in the definition of molar extinction coefficient ε. f can be calculated at various wavelengths, as shown in Table A5.3 below.

Table A5.3 Wavelength variation of the fraction of light absorbed and relative yield of noble metal sensitizers.

λ nm	ϕ(Fe)	f(Pt)	f(Pd)	f(Au)	T glass	Lamp I	Yield Pt	Yield Pd	Yield Au
280	1.24	0.9946	0.8637	0.6605	0.000	0.0000	0.0000	0.0000	0.0000
300	1.24	0.9948	0.8837	0.6023	0.003	0.0029	0.0010	0.0009	0.0016
320	1.23	0.9853	0.8825	0.5483	0.091	0.0489	0.0312	0.0296	0.0473
340	1.21	0.9779	0.9262	0.4790	0.610	0.1897	0.2172	0.2174	0.2897
360	1.20	0.9378	0.9140	0.3563	0.844	0.2644	0.3027	0.3117	0.3131
380	1.17	0.6743	0.6502	0.1992	0.849	0.2414	0.2253	0.2295	0.1812
400	1.15	0.3995	0.3644	0.1164	0.888	0.1466	0.1445	0.1392	0.1146
420	1.10	0.1525	0.1313	0.0382	0.887	0.0575	0.0553	0.0503	0.0377
440	1.05	0.0482	0.0421	0.0114	0.888	0.0316	0.0175	0.0161	0.0113
460	0.95	0.0094	0.0086	0.0022	0.897	0.0144	0.0033	0.0031	0.0021
480	0.92	0.0041	0.0039	0.0010	0.900	0.0029	0.0015	0.0014	0.0009
500	0.88	0.0011	0.0011	0.0003	0.902	0.0000	0.0004	0.0004	0.0002
520	0.66	0.0004	0.0004	0.0001	0.903	0.0000	0.0001	0.0001	0.0001
540	0.25	0.0004	0.0004	0.0001	0.901	0.0000	0.0000	0.0000	0.0000
560	0.06	0.0006	0.0006	0.0001	0.897	0.0000	0.0000	0.0000	0.0000
580	0.01	0.0010	0.0010	0.0002	0.893	0.0000	0.0000	0.0000	0.0000
600	0.01	0.0015	0.0015	0.0004	0.886	0.0000	0.0000	0.0000	0.0000

λ = wavelength in nanometres
ϕ(Fe) = quantum yield of $[Fe(C_2O_4)_3]^{3-}$
f () = fraction of incident light absorbed by a typical sensitizer of platinum (Pt), palladium (Pd), or gold (Au)
T glass = transmittance of a 4mm thick sheet of clear glass
Lamp I = relative emissivity of a Philips actinic/05 UVA lamp
Yield () = λϕfT = relative yield of photoproduct noble metal, not scaled for Lamp intensity distribution

V.2.4 Absorption of actinic light by the printing equipment.

How much UV light at each wavelength is actually arriving at the surface of the print depends on the transmittance of the glass of the printing frame. The following table A5.4 gives for your guidance the UV absorption of windowglass of various thicknesses, so you can assess the light loss in relation to the wavelength emission of any UV source:

Table A5.4. Absorption of UV light by ordinary (window) glass.

Glass Thickness	Wavelength for	50%	30%	10%	transmittance
1 mm		316	312	307	nm
3 mm		330	323	314	
10 mm		352	342	330	

The absorption by Perspex and white crown glass are similar. Pyrex absorbs slightly less. Additionally, any other UV absorbing material in the path, even if apparently clear, can absorb an important part of the actinic light; e.g. plastic masks, and even the negative film base itself, which may have a cutoff in the UV.

All these factors come into play in deciding the overall response of iron-based printing: this qualitative fact has been long known.[87] The best choice of a suitable lamp for printing appears to be that arrived at in Chapter 1, viz., having a spectrum with peak emissivity around 365 nm.

V.3 Theoretical Estimation of Exposure Times

Using the laws of photochemistry summarised above, a theoretical relationship between the exposure and the other parameters of the system can now be derived: the total energy absorbed by the photoactive component over an area, *A,* of sensitizer during an exposure, *It,* is *ItfA*. Now, the energy per photon is hc/λ, so the number of photons absorbed by the photoactive component is $ItfA\lambda/hc$.

If *m* is the number of moles of photoactive component reacted, the number of molecules reacted is *Nm,* where *N* is Avogadro's number. Recalling the definition of the quantum yield, ϕ:

ϕ = no. of molecules reacted / no. of photons absorbed = $Nmhc / ItfA\lambda$

Rearranging this equation we have:

$$It\phi f\lambda = Nhc\ m/A$$

Where the quantities on the LHS (except *t*) depend on wavelength λ as illustrated above:

I is the irradiance in W m^{-2} at wavelength λ

t is the exposure time in s

ϕ is the quantum efficiency of photoactive substance at wavelength λ

f is the fraction of the incident radiation absorbed by the photoactive substance at wavelength λ as calculated and described under 3 above.

(*f* is assumed, for simplicity, to be independent of the exposure – an assumption that will only be valid for small changes – i.e. formation of a 'just perceptible' image, or where there is no self-masking of the image).

λ is the wavelength of radiation in m (assumed monochromatic)

N is Avogadro's number = 6.022×10^{23} mol^{-1}

h is Planck's constant = 6.626×10^{-34} J s

c is the speed of light = 2.998×10^{8} m s^{-1}

m is the number of moles of photoproduct

A is the area of normal surface irradiated in m^2

It is possible to use this relation to calculate the photochemical yield from any source by integrating over the whole waveband of the emission. However, by making a couple of approximations we can reach a rough estimate of the exposures needed.

If the waveband of useful available actinic light is taken as 300–430 nm, we may select a median value of the wavelength as λ = 365 nm, (corresponding with the atomic mercury line, and the maximum emission of most UVA lamps).[88]

Then, inserting values for the physical constants, we have the value of one Einstein, which is the the energy of a mole of photons as:

$$Nhc/\lambda = 3.28 \times 10^{5} \text{ J mol}^{-1} \text{ at } \lambda = 365 \text{ nm}$$

Moreover, if we assume optimum conditions for the absorption of actinic light by setting $\phi = f = 1$ approximately (see values in Table A5.2 above), we get the simple relation between exposure in J m^{-2} and yield of photoproduct in mol m^{-2}:

$$It = 3.28 \times 10^{5}\ m/A \text{ J m}^{-2}$$

If it is further required that all the photoproduct be converted into image pigment;[89] to yield the maximum optical density, the molar yield per unit area must be equal to the original coating weight, W, of the sensitizer, estimated in (3) above:

$$m/A = W = 0.0168 \text{ mol m}^{-2} \text{ for Pt–Pd or } 0.00384 \text{ mol m}^{-2} \text{ for Au}$$

$$\text{Whence } It = 5510 \text{ J m}^{-2} \text{ for Pt–Pd or } 1259 \text{ J m}^{-2} \text{ for Au}$$

For a typical UVA source delivering 50 W m^{-2} at the print surface, bearing in mind that 1 W = 1 J s^{-1}, the times required to make full exposures of such sensitizers (with zero intervening density) are therefore predicted to be 5510/50 = 110 s, or about two minutes for Pt–Pd, and 1259/50 = 25 s, or about half a minute for Au. These predictions are born out well in practice, allowing for the optimistic assumptions that have been made in the theoretical calculation.

Appendix VI Technical Glossary

Excluding specific chemicals (for which see **Appendix I**)
Omitting named photographic processes
Text in **bold face** cross-references to another Glossary entry

Absolute humidity
The actual amount of water vapor present in an atmospheric environment, measured as weight of water per unit volume of air (e.g. in mg/litre). See also **RH** : **Relative Humidity**.

Absorbance
See **Optical Density**

Absorption
Refers to the disappearance of some **wavelengths** of light as it passes through a **homogeneous** coloured medium.

Acid
A substance releasing **hydrogen ions** (H^+) in **aqueous** solution. Acidic solutions have a **pH** value less than 7.

Actinic
Of radiation or light capable of bringing about a chemical reaction; usually confined to the **ultraviolet** and short **wavelength** (blue and green) light.

Adsorption
Refers to the binding of a substance onto the surface of a solid at the **molecular** level.

Albumen
The clear white of hens' eggs: a 10% solution of ca. 40 different **proteins** (**macromolecular polypeptides**). Used as a **colloidal** binder for photographic printing paper of the same name.

Alkali
A substance releasing **hydroxide ions** (OH^-) in **aqueous** solution. Some alkalies achieve this by removing **hydrogen ions** from water and binding them, so leaving excess **hydroxide ions**.
Alkaline solutions have a **pH** value greater than 7.

Ambient
Referring to the properties of the surrounding environment; e.g. its temperature, or **RH**.

Amorphous
A solid not possessing a regular **crystalline** structure, e.g. a glassy substance.

Amphoteric
Capable of acting both as an **acid** and as a **base**.

Anhydrous
Containing no water (when referring to a solid, it means no **water of crystallization**).

Anion
A negatively-charged **molecule** or **atom**; arising through gain of **electron**(s) by the **neutral** entity. Must co-exist with an equal but

oppositely charged atom or molecule; see **cation**. The charge on an anion is always a whole number, written with a superscripted $^{n-}$ (minus) sign, where n is the number of units of charge of the **electron**.

Aqua regia

(Latin: "Royal water" so-called because it is capable of dissolving the "royal" metal, gold.) A mixture of concentrated hydrochloric acid and concentrated nitric acid, in the approximate volume proportions of 3:1.

Aqueous

Watery; usually referring to a **solution** in water.

AR

Abbreviation for AnalaR - Analytical Reagent Grade: a UK designation of a standard of purity in a supplied chemical substance, usually better than 99%. See also **GPR.**

Archival

When applied to photography, the appropriate application of materials, processes and storage to ensure maximum stability and longevity of the image and its substrate.

Atom

The smallest particle of a chemical **element** that retains the essential identity of that element, the **atomic number**.

Atomic Number

A sequential number allocated to each **element**, when they are ordered in the series of ascending **atomic weight** (approximately). It is numerically equal to the number of **protons** in the **nucleus** and therefore the number of orbiting **electrons** in the neutral atom.

Atomic weight

The weight (strictly, mass) of an **atom** of an **element** on a scale relative to the carbon atom having a value of 12.0000. On this scale the oxygen atom has a value of 16.000 and the hydrogen atom 1.008. Now called **relative atomic mass**.

ATR

Attenuated Total Reflectance – for obtaining spectra (UV-Vis or IR) from the surfaces of solids e.g. paper. Cf. Diffuse Reflectance

Avogadro's Number

The number of **molecules** in one **mole** of a substance.
Its numerical value is 6.0221415×10^{23}.

Balance

The chemists name for an accurate weighing instrument. In spite of the traditional icon for 'scales', as seen in the figure of Justice, modern balances only have one pan, and a digital readout.

Base

A substance that reacts with an **acid** to give a **salt**, plus water. All **alkalies** are bases, but not all bases are significantly **alkaline** (e.g. water-insoluble metal oxides).

Bleach

To 'decolourise' i.e. destroy the colour of a substance, making it white, or more nearly so. Some bleaching agents **reduce,** others **oxidise**.

Bond, chemical
Chemical bonding results from the re-distribution of the outermost **electrons** of atoms, which are the least tightly-bound because of their greatest distance from the positively charged nucleus. This re-distribution can amount to a complete transfer of one or more electrons from the **atoms** of one **element** to another, to form **ions**, or, less drastically, a sharing of electrons between atoms- whichever is energetically the most favourable. In the former case chemists speak of **ionic** interactions, and to define the latter, the word **covalent** is used.

Buffer
A substance (or mixture of substances) that helps to maintain a fixed, pre-determined **pH**. The pH value of its solution is only slightly affected by the addition of **acid** or **alkali**.

Buffered paper
Certain types of high quality paper containing a slightly **alkaline** buffer (calcium carbonate = chalk) to neutralise any acid and so enhance their **archival** qualities.

c
Centi-. One hundredth. See **unit prefixes**

cc
Abbreviation sometimes used for cubic centimeters, more correctly written cm^3.

ca.
Abbreviation for *circa* (Latin for 'about'). Indicates that a quantity need only be measured to low precision, of around ± 10%.

Calendering
The process of imparting a smooth and compact surface to paper by passing it through a stack of metal rollers – often heated. Hence ‘hot pressed’.

Callier Effect
The increase of apparent contrast in projection enlarging, compared with contact printing, due to the **scattering** of light by the silver grains in the negative **emulsion**.

Candela
The **SI unit** of luminous intensity.

Carcinogen
A substance known to cause some form of cancer in some species of animal.

CAS
Abbreviation for Chemical Abstracts Service. The CAS Number identifies any chemical uniquely.

Catalyst
A substance that accelerates a chemical reaction, but is left unchanged at the conclusion of it.

Cation
A positively-charged **molecule** or atom; arising by loss of **electron**(s) from the neutral entity. It is written with a superscripted $^{n+}$ sign, where n indicates the number of units of the charge of the **proton** present (equal and opposite to the charge of the electron). See **anion**.

Cellulose
The chief constituent of plant cell walls and therefore of cotton fibers. It can be obtained from materials such as wood pulp and cotton. Chemically, it is a polysaccharide of formula $(C_6H_{10}O_5)_n$, n~15,000.

Celsius
The temperature scale, previously known as Centigrade, C, now replacing the **Fahrenheit**, F, scale throughout the world, except in the USA. The conversion formulae are:
C = 5(F−32)/9 or
F = 32 + 9C/5
Pure water freezes at 0°C (32°F) and boils at 100°C (212°F), under normal atmospheric conditions. Normal room temperature is ca. 20°C (68°F).

Characteristic curve
Also known as the H&D curve or the D/logH curve. The characteristic curve plots the **sensitometric** response of a photographic material. See density and exposure.

Charge
Usually short for electric charge, referring to that on an **ion**.

Chelate
A metal compound, or **complex**, in which the metal **cation** is bound by a **ligand** via two or more atoms of the same **molecule**. It derives from the Greek word for 'crab's claw'.

Chemical Abstracts
A periodical carrying summaries of all recent publications in chemical research. It is the primary literature research tool and aid to finding chemical information.

Chine collé
A print mounting technique in which an image printed on a delicate paper is adhered to a thicker paper for robustness and fine detail.

Chromophore
A chemical group within a molecule that absorbs light over a specific waveband, so imparting a particular colour to that substance.

Clearing
A term used to denote the removal from a photographically printed image of all the excess unreacted chemicals, and reaction products, other than the image substance. It is essentially the same as fixing or fixation.

cm^3
Abbreviation for cubic centimeter. An **SI** measure of volume. Also written as **cc**. It is exactly the same as a milliliter or **ml**.

Coating volume, specific
The volume of liquid taken up per square meter of a paper sheet, under specific conditions of coating, usually in units of cm^3/m^2; the liquid is commonly a photosensitizer solution. See **Cobb value**.

Coating weight
A measure of the surface concentration of a substance (sensitizer or image pigment) as the mass per unit area of a paper sheet (or other substrate). The standard unit is g/m^2

Cobb value
The absorptivity of water by a paper sheet under specified conditions of pressure, temperature and time: the weight of water taken up by a sheet in contact with pure liquid water is expressed in grams per square meter of surface, g/m^2

Cold pressed
In papermaking, having a natural surface texture created by the first pressing between felts. Abbreviated to CP, also called “NOT”, meaning “not hot-pressed” (or HP).

Collodion
A solution of cellulose nitrate dissolved in a 60:40 mixture of diethyl ether and ethanol. The soluble variety of cellulose nitrate is called “pyroxylin” and is less than fully nitrated, which is the case with the explosive, guncotton, which is the tri-nitrate. Collodion is used as a binder layer for photographically sensitized plates and papers.

Colloid
A state of solid matter which is aggregated in very small particles, intermediate between **molecular** dimensions and normal crystals, now called **nanoparticles**. Colloids have a particle size smaller than the wavelength of visible light. The term 'colloid' is also applied to 'gluey' substances, **macromolecules** such as gelatin.

Complex
A chemical compound formed from one or more **ligands** binding with a metal **cation**. Also called a **coordination compound**.

Complexing agent
Another name for a **ligand**.

Compound
The result of two or more **elements** entering into chemical combination. See **Bond, chemical**.

Concentration
In general, the relative amount of one substance dispersed within a perfectly **homogeneous** mixture. Most commonly, it applies to solutions in water or other liquids and can be measured in several different ways: %w/w; %w/v; %v/v; molarity.

Contrast
Of a photographic image, or photographic material developed under specified conditions. Measured by the slope of the **characteristic** curve.

Coordination number
The number of nearest neighbour **atoms** to the central atom or **ion** in a coordination compound or **complex**, or in a crystal lattice.

Corning™ glass
Heat-resistant glass, used for cookware and chemical equipment such as flasks and beakers. The equivalent in the UK is **Pyrex™ glass**.

Covalent
See **Bond, chemical**.

Crystalline
A solid that has a regular repeating lattice structure of **atoms**, **molecules** or **ions**.

D/logH curve
See **characteristic curve**.

Deckle edge
The rough chamfered edge formed naturally on a sheet of mold-made paper.

Decolourise
See **bleach**.

Deliquescent
Property of a solid having a tendency to absorb water from the atmosphere, and then to dissolve in it, to form a **solution**.

Densitometer
An instrument for measuring **optical density**.

Density
The property of a substance expressed by its mass per unit volume. The usual units are g/cm^3. See also **optical density**

Density range
The difference in **optical density** between the lightest and darkest parts of an image.

Desiccant
An inexpensive substance that readily absorbs water from the atmosphere, such as anhydrous calcium chloride or silica gel. Used to create a dry chamber e.g. for the storage of sensitized but unexposed papers.

Developer
A mild **reducing** agent (usually an organic amine) which is capable of reducing the exposed silver halide grains constituting a **latent image**, entirely to silver metal.

Developing-out
A photographic printing process in which the **latent image** of an exposed sensitized paper is converted into a visible image by a chemical developer.

Development
The process of transforming the **latent image** in exposed silver halide grains entirely to silver metal, thus producing the final, visible photographic image, with an amplification of the effect of light by a factor of ca. 10,000,000. The parameters defining development are: developer type, concentration, temperature, time, and agitation.

Diapositive
A positive transparent photographic image on plastic film base or glass.

D_{max}
See **maximum density**

EDX
See **SEM-EDX**

Effervescence
The dignified word to describe the evolution of a gas, as bubbles, from a liquid, i.e. ‘fizzing’.

Electrochemical Series
An ordering of the metallic elements according to their increasingly **electropositive** character. A metal higher in the series can, by passing

into solution as **cations**, displace a metal lower in the series from combination in its salts.

Electron
The fundamental particle of negative electrical charge.

Electronegative
Having a tendency to attract or gain **electron(s)** to form an **anion**. The most electronegative elements are the halogens, and oxygen.

Electropositive
Having a tendency to lose **electron**(s) readily to form a **cation**. The most electropositive elements are the alkali metals such as sodium. The least electropositive metals are the noble metals like gold and platinum.

Element (chemical)
A fundamental constituent of matter that cannot be split into simpler constituents by chemical means (i.e. at low energies). Consisting of one type of **atom** only, with a characteristic **atomic number**. See **Periodic Table**.

Emulsion
Small droplets of one liquid suspended and distributed throughout another, **immiscible** liquid. Compare **suspension**. The word is also used widely (but incorrectly) to describe the suspension of silver halides in gelatin used to make photographic films and paper.

Equilibrium (chemical)
The state of being incapable of further (chemical) reaction.

Equimolar
Having equal amounts or concentrations on the molar scale of two chemical components, i.e. equal numbers of molecules.

Excess
A quantity exceeding that needed to complete a balanced chemical reaction.

Exposure (photographic)
Intensity of light multiplied by the duration.
Exposure = **Illumination** x time.
Usually given the symbol H, the units of exposure are **lux** seconds.

Exposure scale (or Exposure range)
Of a photographic material: the number of **stops** of **exposure** needed to transform it from the minimum **optical density** (usually white) of the paper base to the **maximum density** (black or other colour).
It may also be expressed as a $\log_{10}$(Exposure) value, where a change of 0.3 =1 stop.

Fahrenheit
An earlier temperature scale, F, still used in the USA. See **Celsius**.

Formula (Chemical)
The relative numbers of **atoms** of the **elements** making up the composition of a pure substance, written in chemists' shorthand form using the symbols for the chemical **elements**.
See also **molecular formula**.

Formula weight
The sum of the **atomic weights** of all the **atoms** making up the **formula** of the substance; also known as **relative molecular mass**.

FTIR

Fourier Transform Infra-Red Spectrometry can identify the functional groups present in molecular species, by their characteristic bond-stretching and angle-bending vibration frequencies which absorb radiation in the **infrared** region of the spectrum. It is especially effective for providing "fingerprints" of polar functional groups formed by the lighter elements, *i.e*. organic molecules, such as oxalates, and can be applied to the study of surfaces to identify coatings on paper.

Functional group

In chemistry, a small group of bonded atoms in a molecule, having a specific composition and structure that impart a characteristic reactivity.

G

Abbreviation for Giga- one billion times. See **unit prefixes**.

g

Abbreviation for **gram**(s) the **SI** unit of mass (or, loosely, weight).

GCMS

Gas Chromatography and Mass Spectrometry provide a precise characterization of volatile (organic) species present in samples such as paper sizing or coating agents. **LC-MS** is similar in principle – but using liquid phase chromatography.

Gel

A solidified mass ("jelly-like") of a **colloidal** (**macromolecular**) substance, not having any regular **crystalline** structure.

Gelatin

A very complex organic **macromolecular** material (a **protein**) obtained from animal skins and bones, and used as a **colloidal** binder in the preparation of photographic **emulsions**, and for **sizing** some papers. Gelatin has a very large capacity to 'protect' **nanoparticle** gold.

GPR

Abbreviation for General Purpose Reagent. A UK specification of a degree of purity in a supplied chemical substance, usually in the range 95-99%. Contrast with **Analar**.

In the USA a similar designation is SLR for Standard Laboratory Reagent or ACS reagent for American Chemical Society.

gr

Abbreviation for grain(s), an obsolete unit of weight seen only in old recipes. Avoid confusing it with grams. 1 gr = 0.0648 g

Gradation

Usually refers to tonal gradation: the visible separation of areas of perceptibly different **optical density** in an image.

Graduate

In the USA, a measuring cylinder, usually of glass, graduated by volume.
In the UK, one who has been awarded a university degree.

Graduations

On chemical glassware: the marks to indicate the volumetric calibration, or on a thermometer to indicate temparature.

Gram

The **SI** unit of mass – an amount of matter (or, loosely, weight).

Grey card
The standard neutral mid-grey optical reflectance of 18% = **optical density** of 0.72, usually on a card substrate.

gsm
Abbreviation sometimes used for grams per square meter, g/m^2. See **paper weight**.

H&D Curve
Hurter & Driffield curve. See **characteristic curve.**

Hardening
Of **colloids** such as **gelatin** or gum: the process of rendering them insoluble in water – also resembles tanning.

Homogeneous
Uniform throughout, with no internal boundaries or surfaces – consisting of a single phase, either solid, liquid, or gas.

HP
Abbreviation for Hot Pressed. A term used to describe the smooth surface finish of a paper which has been pressed between heated metal plates or rollers in the final stages of the manufacturing process – called '**calendering**'.

Humectant
A substance that tends to attract moisture. See **hygroscopic**.

Humidify
To take up water vapour from the atmosphere.

Hydrate
(verb) To allow to take up water, often from the vapour. To humidify.
(noun) A solid containing **water of crystallization**. An hydrated salt.

Hydration
The process of taking up or absorbing water.

Hydrogen ion
The **ionised** hydrogen **atom** H^+. Since this is a bare **proton**, it will attach itself to the most available **molecule**, e.g. with water forming the hydronium ion H_3O^+, or with ammonia forming ammonium ion H_4N^+.

Hydrolysis
Decomposition of a substance by water or **alkali**. In the case of a metal salt, to give the metal hydroxide or (sometimes) oxide.

Hydrometer
A device for measuring the relative **density** (specific gravity) of liquids by means of the partial immersion of a calibrated float.

Hydrophilic
Having an affinity for water.

Hydrophobic
Having the property of repelling water.

Hygrometer
An instrument for measuring relative humidity (**RH**) in the air.

Hygroscopic
Tending to absorb water from the atmosphere. See **deliquescent**.

Hypo
Abbreviation for 'hyposulphite of soda', the obsolete (C19th) chemical name, still employed by some photographers, for sodium thiosulphate.

Hypo Clearing Agent
A proprietary mixture to increase the speed and efficiency of the washing of fixed silver-gelatin photographic materials. With platinum-palladium and gold printing, the agent aids the clearing of residual iron compounds. (Proprietary names include Ilford Washaid™, Permawash™, and Speedwash™). It consists mostly of sodium sulphite and disulphite.

Illumination
Also called Illuminance. The **luminous flux** falling upon unit area of a surface. The **SI** unit of illumination is the **lux**.

Immiscible
Two liquids not capable of mixing with each other to give a single phase; they separate, leaving a physical boundary.

Infrared
Electromagnetic radiation having wavelengths slightly longer than visible light, i.e. greater than about 750 nm to about 1 mm. Infrared radiation is responsible for radiant heat.

Intensification
A process intended to increase the contrast or density range of a print or negative, usually by chemical deposition of extra image substance.

Ion
A **molecule** or **atom** that carries an electric charge, due to gain or loss of **electrons**. The charge is written superscripted following the chemical symbol, e.g. Fe^{3+}. See **anion** and **cation.**

Ionic
A chemical compound that owes its chemical **bonding** force to the attraction between unlike electric charges, e.g. common salt, sodium chloride, formula NaCl, is more accurately described as the ionic compound $Na^{+}Cl^{-}$.

Ionization
The process of forming **ions**, usually in **solution**.

IR
Abbreviation for **infrared**

IUPAC
International Union of Pure and Applied Chemistry. The international body responsible for recommendations concerning chemical notation and nomenclature.

Joule
The **SI** unit of energy, or work, abbreviated to J. 1 **Watt** = 1 Joule/sec.

k
Kilo-. One thousand times. See **unit prefixes**.

Laminar structure
Having a layered structure – particularly in the context of photographic prints on paper, which are characterised as having one, two or three layers.

Latent image
The initial effect of light on a crystal of silver halide, to produce a sensitivity speck consisting of a few atoms of silver, which makes the whole crystal **developable** by reduction into a grain of silver. The latent image is invisible to the naked eye.

lbs
Abbreviation for pounds weight. See **paper weight**.

LD50
Abbreviation for Lethal Dose 50% of the population. An index of the toxicity of a substance, usually expressed as a mass of the substance per kilogram of body weight of the experimental animal, which when dosed will result in the death of half the experimental population.

Ligand
A **complexing** agent, i.e. any **molecule** capable of binding chemically to a metal **cation** to give a molecular compound called a metal complex.

Lignin
A component of the cellular structure of wood. It is a complex, polyphenolic **macromolecule**, susceptible to **oxidation** and discolouration.

Litre
Spelt 'liter' in the USA. A commonly-used, but non-**SI** unit of volume, equal to 1000 cm^3 = 1 dm^3.

Logarithm
The logarithm of a number (to a specified base: 10 is most commonly used) is written as $\log_{10}X$. It is equal to the power to which the base must be raised to give that number:
$10^{(\log_{10}X)} = X$. When numbers are multiplied, their logarithms must be added.

Lumen
The **SI** unit of luminous flux.

Luminous flux
The amount of light passing through a given area per second measured in **lumens**.

Luminous intensity
Measured in **candelas**.

Lux
The **SI** unit of **illumination** or illuminance: equal to the **luminous flux** falling upon a unit area of one square meter. 1 lux = 1 lumen/m^2
In the USA the non-**SI** unit used is the footcandle (= 10.76 lux)

Macromolecule
A large **molecule** (of high molecular weight) consisting of many smaller molecular units, which may differ, chemically **bonded** together. The repetition of units may be irregular. Compare with **polymer**.

Maximum density
Often called D_{max}: The highest value of **optical density** that is present in an image, or that a given photographic material can yield.

m
Milli-. One thousandth of. See **unit prefixes**.

M
Mega-. One million times. See **unit prefixes**.

µ
Micro- (Greek letter mu). One millionth of. See **unit prefixes**.

mg
Milligram. One thousandth of a gram.

mil
One thousandth of an inch.

ml
Millilitre. One thousandth of a **litre**. One ml = one cc or cm^3.

Modulation Transfer Function
Abbreviated as MTF. A detailed measure of the resolving power of a photographic imaging material.

Molarity
The **concentration** of a **solution** expressed as the number of **moles** of **solute** that are present in one **litre** of the solution. The molarity of a substance is indicated by placing its formula within square brackets [X].

Molar ratio
The relative proportions of two substances expressed in terms of their respective numbers of **moles**, i.e. their relative numbers of **molecules**. It is then obvious why chemicals generally react or combine in simple proportions when expressed as molar ratios.

Mole
The chemist's unit to measure the amount of a pure substance. A mole of any substance is equal to the **formula weight** or **relative molecular mass** measured in grams. It is more fundamental than just weight or mass, because one mole of any substance always contains the same number of **molecules** (called **Avogadro's number** = 6.022×10^{23}).

Molecular formula
The chemists shorthand designation to identify a pure substance, which gives the numbers of **atoms** of the different chemical **elements** combined within its **molecule**, and sometimes an indication of the way they are **bonded** together.
See structural formula.

Molecular weight
Another name for **formula weight**. Now more correctly referred to as **relative molecular mass**.

Molecule
The smallest and simplest particle of a chemical substance or compound that can exist and still retain the identity of the whole. Molecules are composed of **atoms** chemically **bonded** in fixed proportions, and have definite 3-dimensional shapes.

Monomer
A single **molecular** unit. Compare **oligomer** and **polymer**.

MSDS
Acronym for Material Safety Data Sheet, providing information for the safe handling of chemicals, and their associated hazards. MSDS are now called SDS (Safety Data Sheets) under the Globally Harmonized System.

Mutagen
A substance known to cause mutations in the germ cells.

Mylar™
Also known as Melinex™. A clear archival polyester film, available in various thicknesses. The type most suitable for placing between the negative and the sensitized paper is the 20 micron Type D, made by Secol Ltd.

n

Nano-. One billionth (US) of: 1/1,000,000,000. See **unit prefixes.**

Nanoparticle

A particle of a substance having a size intermediate between that of **atoms** and that of the **wavelength** of visible light, i.e. in the region of 1 to 100 **nm**. See **colloid**.

Neutral

(Chemistry) Neither **acid** nor **alkaline**. Neutrality prevails when the hydrogen **ions** and **hydroxide** ions in a water solution are equal in number. i.e. pure water is neutral, having **pH** 7.
(Physics) Having no electric charge.

nm

Abbreviation for nanometer, one billionth (10^{-9}) of a meter. A unit of length convenient for measuring the **wavelength** of visible light, which spans the region of the spectrum between 400 nm (violet) and 750 nm (deep red).

Noble Metal

Alchemical name for metals which are substantially unchanged by fire; i.e. metallic elements that resist oxidation and corrosion, such as platinum, palladium, gold, and silver.

Numerical prefixes

The prefixes used in chemical names to indicate the numbers of **atoms**, **molecules,** or **functional groups** of a given type are as follows:
Mono- 1; Di- 2: Tri- 3; Tetra- 4; Penta- 5; Hexa- 6; Hepta- 7; Octa- 8; Nona- or Ennea- 9; Deca- 10.

Oligomer

A **molecule** formed by the repetition of several of the same molecular unit **bonded** chemically together a few times over. Contrast with **polymer** and **monomer**.

Opacity

The ratio of the intensity of the light falling on an object to that passing through it. (Define geometry and wavelength response)

Opacity = Intensity of Incident / Transmitted light = I_o/I_t

It is the reciprocal of the **transmittance**, I_t/I_o.

Optical density

Given the symbol D, and referred to in photographic contexts simply as density, it is defined as the logarithm (to base 10) of the **opacity**:

$$D = \log_{10}(I_o/I_t) \quad \text{or} \quad 10^D = I_o/I_t$$

where I_0 is the intensity of incident, and I_t of transmitted, light.
Optical density has no units (i.e. it is a dimensionless number). Optical densities of superimposed layers are *additive*, whereas **transmittances** and **reflectances** or **opacities** must be *multiplied*.
Three conditions of measurement must be defined for optical density: the geometry of the light beam may be specular, diffuse or doubly diffuse; and the **wavelength** response of the photoreceptor may be spectral, visual (photoptic), printing, or arbitrary. Also, density may be measured in **transmittance** or **reflectance** modes. Thus there are 24 different types of optical density. 'Diffuse visual density' is most used in photography.

Optical density range
The difference between the highest and lowest **optical densities** of a negative or print. Often just called the 'density range'.

Orthochromatic
A photographic film which does not respond to light of the red region of the spectrum.

Osmosis
The process of the diffusion of **solvent**, but not **solute**, through a semi-permeable membrane. The solvent will diffuse in the direction of highest solute concentration, to dilute the solution.

Oxidation
The removal of **electrons** from an **atom** or **molecule**, in consequence of which it becomes more positively charged (or less negatively charged). An increase in the **oxidation state** of an **atom** or **ion**. Contrast with **reduction**.

Oxidation state
A formal electric charge that may be assigned to an **atom**, either free or bound in a **molecule**, which is calculated by the number of **electrons** it has effectively lost, compared with the neutral atom. Shared electrons are always formally allocated to the more **electronegative** of any two **bonded** atoms.
The oxidation state is written, in parentheses, and in capital Roman numerals, following the name or symbol of the **element**: e.g. iron(III), or Fe(III), and pronounced "iron-three".

Panchromatic
A photographic film which responds to all the **wavelengths** of light of the visible spectrum.

Paper weight
A measure (thickness x density) of a paper sheet. Its units are weight per unit area: g/m^2 (sometimes written as gsm). In the USA, paper weights are sometimes given in lbs (imperial pounds weight per ream of ca. 500 sheets) but this is an unspecified measure, which depends on the sheet size. For imperial-sized sheets (30 x 22 inches) the relationship is:

Weight in gsm = 2.13 x weight in lbs.

Parchmentization
A treatment for **cellulose** paper with strong **acid** (usually concentrated sulphuric acid) which renders it translucent and rather brittle, resembling parchment. It destroys the regular crystalline structure of the fibres and renders the cellulose surface **amorphous.**

Periodic Table
A sequential arrangement of all the known **elements**, in order of increasing **atomic number**, in which elements having similar outer **electron** configurations, and therefore similar chemistry, are tabulated in the same vertical column or Group. The number of elements in each successive row of the Periodic Table is 2, 8, 8, 18, 18, 32, 32 .
Each commences with an alkali metal and terminates with an inert gas. All 118 known elements have now been identified and named by **IUPAC**.

pH

A measure of the **acidity** or **alkalinity** of a solution. It is equal to the logarithm (to base 10) of the reciprocal of the **hydrogen ion** molarity:

$$pH = \log_{10}(1/[H^+]) \text{ or } pH = -\log_{10}[H^+]$$

Neutrality in water corresponds to pH 7; acidic solutions have smaller, and alkaline solutions greater pH than 7, with a range usually lying between 0 and 14. Every unit *decrease* in the pH represents a ten-fold *increase* in the acidity.

Photoceramic

A photographic image formed upon, or transferred to, a ceramic substrate, and often fired under a glaze to render it highly permanent.

Photochemical

A chemical change brought about by the absorption of light.

Photogram

A photographic image formed on a light-sensitive surface by the shadow cast by an object in direct contact with it. I.e. there is no lens to form the image.

Photon

The fundamental particle of light, and of electromagnetic radiation in general.

Photoproduct

A chemical substance produced by a **photochemical** reaction.

Photosensitive

Capable of responding to light by undergoing some physical or chemical change.

Pipette

A calibrated glass tube used for the controlled delivery of small accurately-measured volumes of liquids.

Polyester

A form of inert plastic **polymer** used in transparent sheets for **archival** sleeves for negatives and prints.

Polymer

A **macromolecule** formed by the regular repetition of one (or, in the case of a co-polymer, two) **molecular** unit(s), **bonded** chemically together many times over.

Polypeptide

A class of **macromolecules** which consist of polymeric chains of amino-acids linked together by a peptide bond -CONH-. See **protein.**

Precipitate

An insoluble solid thrown out of a **solution** due to a chemical reaction resulting in formation of a **supersaturated** solution.

Printing-out

A phenomenon in which the photographic image appears during the exposure due to the action of the light alone. Printing-out materials require a very heavy exposure, compared with the development of a **latent image** in silver halides by chemical reaction with a **developer** after the exposure.

Protein
Large biomolecules consisting of one or more long chains of **polypeptide**. See **albumen** and **gelatin.**

Proton
A fundamental positively-charged particle, the nucleus of the hydrogen **atom**, i.e. the **hydrogen ion**, H^+. Its charge is equal, but opposite in sign to that of the **electron**.

Pyrex™ glass
Heat-resistant glass, used for cookware and chemical equipment such as flasks and beakers. The equivalent in the USA is **Corning™ glass**.

Quantum Yield
Also called Quantum Efficiency. In a **photochemical** reaction: the average number of **molecules** transformed by the absorption of one **photon**.

Rag paper
Originally used to describe paper which was manufactured from recycled cotton and linen rags, and therefore consisted almost entirely of **cellulose**. The term is now obsolete owing to the contemporary use of cotton and linen fibers derived directly from the plants.

Raman Spectroscopy
Raman spectroscopy uses the modification of the wavelength of scattered light, usually in the visible region. It provides information on molecular vibration frequencies, and is often complementary to infrared spectrometry, because it is strongest in detecting highly polarizable groups formed by heavier atoms, and having lower vibration frequencies, i.e. inorganic complexes.

Reagent
A pure chemical, usually dissolved in a **solvent** (in solution) – often water – at a **concentration** suitable to perform a test or carry out a reaction.

Redox Potential
The voltage that 'drives' the tendency of a **redox** couple to transfer **electron**(s).

Redox Reaction
A **red**uction-**ox**idation reaction, involving the transfer of **electrons** from one atom, molecule, or ion to another.

Reduction
The addition of **electrons** to an **atom** or **molecule**, in consequence of which it becomes more negatively charged (or less positively charged). It brings about a decrease in the **oxidation state** of an atom or ion. Contrast with **oxidation**.
The word reduction is also used in photography to denote a process of diminishing the **optical density** of an image by dissolving away some of its substance. It is an unfortunate source of confusion that such a process is, chemically speaking, an **oxidation** (e.g. of silver metal).

Reflectance:
The ratio of the **intensity** of the light reflected diffusely from an object to that falling on it.
Reflectance = Intensity of Diffuse Reflected light / Incident light = I_r/I_o

Reflection density

The definition is analogous to that of **optical density** in **transmittance**: reflection density is the logarithm (to base 10) of the reciprocal of the reflectance:

$$D = \log_{10}(I_o/I_r) \text{ or } 10^D = I_o/I_r$$

where I_r is the intensity of light reflected diffusely (scattered) by the surface. The term is used to describe tonal values in a print.

Refractive index

Also known as refrangibility. A measure of the ability of a substance to 'bend' a ray of light away from its original direction.

Relative Atomic Mass

Abbreviated to RAM. The mass (loosely, weight) of an **atom** of an **element** on a scale relative to the carbon atom as 12.0000. Also called **atomic weight**.

Relative Humidity

Abbreviated to **RH**. The ratio, defined as a percentage, of the amount of water vapor present in the atmosphere to the amount that would have been present if the same atmosphere were saturated (i.e. contained all the water-vapor it could hold) at that temperature.

Relative Molecular Mass

Abbreviated to RMM. The sum of the **relative atomic massess** of all the **atoms** making up the **molecular formula** of the substance. Also called **molecular weight** or **formula weight**.

Reversal

A **sensitometric** response in which the **optical density** diminishes with increasing **exposure**. See **solarization**. Also a method of processing a photographic material in a positive-working sense.

Salt

Any substance composed of **cations** and **anions**; i.e. an **ionic** compound. "Common salt" is sodium chloride: Na^+Cl^-.

Saturated solution

A **solution** that cannot contain any more **solute**, at a specified temperature. Marked by the presence of excess solid in contact with it.

Scattering

When referring to light: essentially the reflection of light in many different directions by many small particles of substance. Contrast with **absorption**.

SEM-EDX

Scanning Electron Microprobe with Energy Dispersive X-ray spectrometry. An analytical technique using an electron microscope's beam of electrons to excite the characteristic X-ray spectra of the **elements** present. The sample must be small (~cm) so it may be effectively a 'destructive' technique, but it is carried out in vacuo, so has the advantage over **XRF** that light elements can also be detected, and the area analysed can be imaged at high magnification.

Sensitizer

The **solution** (usually **aqueous**) of light-sensitive chemicals that is coated onto a paper (or other surface) to make a photographic printing material.

Sensitometry
The assessment of **photochemical** response in a photographic material, by **exposure** to a measured **illumination** for a given time, and then measurement of the **optical density** of the image formed, under specified processing conditions.

SI Units
See **Système Internationale**.

Siderotype
A collective name, originally due to Sir John Herschel, for all the iron-based photochemical printing methods.

Silver-gelatin
A term used to describe photographic printing papers that have been coated with a photographic **emulsion** – the incorrect, but widely used, term for a **suspension** of silver bromide and/or chloride in gelatin.

Size or sizing agent
A glutinous preparation (usually gelatin or starch) used to treat paper or fabric to reduce its absorbency. Some sizing agents, such as resins and **alkylketene dimers** (e.g. Aquapel™) are **hydrophobic** (water-repellent).

Sol
A **suspension** of a particulate **colloid** in a liquid. If the liquid is water, it is called a hydrosol.

Solarization
A photographic phenomenon in which increasing **exposure** causes a diminution in the **optical density** of the image – also called **reversal**.

Solubility
The maximum weight of the substance that will dissolve completely in a given volume of **solvent** at a prescribed temperature. Usually given in units of g/100 cm^3 of solution, or g/100 cm^3 of solvent. N.B. these differ. The weight of substance needed to make 100 cm^3 of **saturated solution**.

Solute
The substance which is dissolved in a **solvent** to make a **solution**.

Solution
A liquid which has another substance(s) dissolved in it. True solutions are always clear i.e. they do not perceptibly scatter light (though they may absorb it, i.e. be highly coloured). Contrast with a **suspension**.

Solvent
A liquid capable of dissolving other substances (solid, liquid or gaseous) to form **solutions**.

Spatula
A chemists' tool for dispensing small amounts of solids; usually a small, shaped strip of inert plastic or nickel-plated metal or stainless steel. Spatulas come in many shapes and sizes.

Stalagmometry
The study of surface tension by measuring the weight of drops of liquid.

Step tablet
A grey scale consisting of defined regions of uniformly increasing **optical density**. Used in photographic **sensitometry** to determine correct exposure, and to plot the **characteristic curve** of the medium.

Stoicheiometric
In exact quantitative chemical relationship: usually simple proportions.

Stop
In photography, one stop more is a doubling, and one stop less a halving of the **exposure**. The term is also used to describe differences in **optical density**: one stop = difference in optical density of 0.3 This corresponds to a doubling or halving of the **transmittance** or **reflectance** (because $\log_{10}2 = 0.301$).

Structural formula
The **molecular formula** drawn out so as to indicate how the constituent **atoms** are connected by chemical bonds to one another in space.

Supersaturated
A solution, at a specified temperature, that contains more **solute** than is permitted by the equilibrium **solubility**. If scratched, jarred or 'seeded', it may rapidly crystallise.

Surfactant
An agent that greatly reduces the surface tension of a liquid (usually water), enhancing its ability to wet objects, or penetrate the **cellulose** fibres of paper. E.g. Tween™ 20.

Suspension
Small particles of an insoluble solid dispersed in a liquid or a gel.

Système Internationale
Abbreviated to **SI.** A rationalized system of **units** of physical measurement now agreed worldwide and used by scientists to the exclusion of all previous systems. The seven basic physical quantities (from which all others can be derived), their units, and abbreviations:

Quantity	Unit	Abbreviation
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampère	A
temperature	kelvin	K
luminous intensity	candela	cd
amount of substance	mole	mol

Tare
In weighing out a substance: the weight of the container or receptacle which must be deducted from the total.

Teratogen
A substance known to cause congenital (birth) defects, i.e. in the development of the embryo of any animal.

Tonal range
The **optical density range** of a print, seen visually from light to dark.

Toning
The application of a reactive chemical to a photographic print with the intention of changing the final colour of its image.

Transmittance
The fraction of the incident light passing through an object.

$$\text{Transmittance} = \frac{\text{Intensity of Transmitted light}}{\text{Intensity of Incident light}} = I_t/I_o = 10^{-D}$$

It is the reciprocal of the **opacity**, I_o/I_t.
Transmittance is sometimes expressed as a percentage: 100 I_t/I_o %

Unit prefixes

The following **SI** abbreviations, used as prefixes, indicate the fractions or multiples of the unit quantity they attach to:

n	nano	one billionth	0.000000001	10^{-9}
µ	micro	one millionth	0.000001	10^{-6}
m	milli	one thousandth	0.001	10^{-3}
c	centi	one hundredth	0.01	10^{-2}
d	deci	one tenth	0.1	10^{-1}
D	deca	ten	10	10^{1}
K	kilo	one thousand	1,000	10^{3}
M	mega	one million	1,000,000	10^{6}
G	giga	one billion	1,000,000,000	10^{9}
T	tera	one trillion	1,000,000,000,000	10^{12}

UV

Abbreviation for ultraviolet. Electromagnetic radiation with wavelengths from 400 nm to about 50 nm. Conventional divisions of the ultraviolet spectrum are:
UVA 400–315 nm; UVB 315–280 nm; UVC 280–200 nm.
The so-called 'near ultraviolet' UVA is the most suitable actinic radiation for siderotype (iron-based) printing processes.

Vellum

Originally, a parchment made from the bleached and scraped skin of a calf, but in modern papermaking it denotes an entirely vegetable sheet in which the cellulose paper pulp is heavily beaten to produce a translucent or even semi-transparent sheet: "tracing paper".

Water of Crystallization

Water **molecules** incorporated in the crystalline lattice of a solid substance.

Watermark

A mark or legend imparted to a paper sheet by thinning it during manufacture with a wire design attached to the screen. Generally used to identify the papermaker, surface, format or date.

Watt

Abbreviated to W. The **SI** unit of power, the rate of doing work, or the rate of transfer of energy. 1 Watt is equal to one **Joule** per second.

Wavelength

The property of light that determines its hue: the distance between successive crests (maxima) of the waves of electromagnetic radiation. Conveniently expressed in **nanometer** units of length, the following typical wavelengths represent the colours of the spectrum:
red 700, orange 620, yellow 580, green 530, blue 470, violet 420 nm.
The concept extends to all electromagnetic radiation, beyond the limits of visibility (400–750 nm). The shorter the wavelength, the higher the intrinsic energy of the radiation. See **ultraviolet** and **infrared**.

Weight of paper

See **paper weight.**

Wetting agent

See **surfactant**.

XRF

X-Ray Fluorescence spectrometry. Non-destructive analytical technique to identify the heavier elements – usually of **atomic number** greater than 18 (argon) – present in a sample, unless a helium gas flush is used to displace the atmosphere in the intervening path between X-ray source and sample. It does not identify the elements' state of chemical combination. The method as usually applied is only semi-quantitative.

Notes and References

[1] The convenient collective noun for all the iron-based processes; long-forgotten, and now revived. It was first coined by Sir John F.W. Herschel from the Greek word for iron, sideros, σιδηρος.

[2] Mike Ware, 'Platinum Reprinted', *British Journal of Photography*, **133** (41), 1165-1167, (10 October 1986); **133** (42), 1190-1194, (17 October 1986).

[3] Mike Ware, 'The Argyrotype Process', *British Journal of Photography*, **138** (6824), 17-19, (13 June 1991).

[4] Mike Ware, 'A New Blueprint for Cyanotypes', *Ag+ Photographic*, No. 7, (1995) pp 74-80.

[5] https://www.mikeware.co.uk

[6] The possible effects of the CO_2 gas evolution during exposure are fully worked out in this essay:

https://www.mikeware.co.uk/

[7] 1 µm is one micron or micrometer – one millionth of a meter (m), or one thousandth of a millimeter (mm). For the benefit of those still addicted to Imperial measure: 1 m = 39.37 inches and 1 µm = 0.03937 thousandths of an inch ('thou'), or 25 µm ≈ 1 'thou' (sometimes confusingly called 1 'mil' in the USA).

[8] 1 nm is one nanometer – one billionth of a meter, or one millionth of a millimeter.

[9] The internal filter effect is the absorption of actinic light by a component of the sensitizer that is not photoactive. These long wavelength lamps may be fairly effective for chrysotype, because at the 420nm wavelength there is little or no 'internal filter' effect due to the lack of absorption by the colourless gold(I) complex.

[10] Sandy King, 'Ultraviolet Light Sources for Printing with the Alternative Processes'; http://unblinkingeye.com/Articles/Light/light.html

[11] From a point source of light, Intensity is proportional to $1/\text{distance}^2$ i.e. when the distance is doubled, the intensity becomes one quarter, etc.

[12] D.C. Pritchard, *Lighting*, Longmans 1990, 30-7, 90.

[13] Judy Seigel, 'A Good Hot Spot is Hard to Find', *Journal of Post-Factory Photography,* 7 (January 2002) 39-40.

[14] Luis Nadeau, *History and Practice of Platinum Printing*, Fredericton: Atelier Luis Nadeau, 1994.

[15] Judy Seigel, 'Light Carpentry', *Journal of Post-Factory Photography*, 6 (May 2001) 20-22; Don Bryant, 'Build your own UV Printer', *Journal of Post-Factory Photography,* 5 (August 2000) 43.

[16] Dick Stevens, *Making Kallitypes*, Boston: Focal Press, 1993.

[17] WHO ref

[18] Although its implication as a cause of the skin cancer, melanoma, is revising this view.

[19] Lignin is a complex, crosslinked polyphenolic macromolecule, of approximate empirical composition $C_{10}H_{11}O_4$.

[20] The polyphenols are oxidised to quinones, which provide the colour – the reaction is essentially similar to that causing the discolouration of photographic developers.

[21] Dard Hunter, *Papermaking*, New York: Dover 1978; Richard L. Hills, *Papermaking in Britain 1488–1988*, London: Athlone Press 1988; Francis Bolam (Ed.), *Paper Making*, London: Technical Section of the British Paper and Board Makers' Association, 1965; S. Carter Gilmour (Ed.) *Paper: the Paper Merchants Textbook*, London: Longmans, Green & Co Ltd., 1965.

[22] Dard Hunter, *op. cit.* 136–8.

[23] $Al_2(SO_4)_3 + H_2O \rightarrow Al(H_2O)_6^{3+} \rightarrow Al(OH)(H_2O)_5^{2+} + H^+$

[24] If cellulose is simply represented by Cell–OH the chemical reaction is:

$$2RHC{=}C{=}O \rightarrow RHC{=}C{-}O + Cell{-}OH \rightarrow RCH_2CO{-}CHR{-}CO{-}O{-}Cell$$
$$\qquad\qquad\qquad\qquad\quad |\ \ |$$
$$\qquad\qquad\qquad\qquad RHC{-}C{=}O$$

Alkylketene → alkylketene dimer + cellulose → alkyl β–keto ester of cellulose

Where alkyl = R = $C_{16}H_{33}$ (hexadecyl or cetyl)

[25] The commercial solution usually sold as "formalin" is 40% w/w formaldehyde, so this should be diluted 20 times to make the 2% hardening bath.

[26] Glyoxal has the formula $(CHO)_2$. It is also available as a 40% aqueous solution. Recently, an alternative agent, glutaraldehyde $OCH(CH_2)_3CHO$ has been suggested.

[27] At 20°C, there is risk of mould growth above 74% RH; at 35°C the onset is at 70% RH.

[28] This is a co–polymer: polyoxyethylene sorbitan monolaurate.

[29] John A. Spencer, 'Instrument for Spreading Solutions', *Journal of the Photographic Society,* 7 (21 July 1853) 88–9; Joseph Sidebotham, 'The Printing Process in Photography', *Recreative Science* 2, London: Groombridge and Sons 1861, 120; Marcus Sparling, Ed. James Martin, 'The Theory and Practice of the Photographic Art', *The Circle of the Sciences: 7 Practical Chemistry*, London: Griffin, Bohn and Co., 1856, 142.

[30] R.C. Weast, Ed., *Handbook of Chemistry and Physics,* Florida: Chemical Rubber Company Press Inc, 1980, Table E–46; F.E.M. O'Brien, 'The Control of Humidity by Saturated Salt Solutions', *Chemistry and Industry,* 25 (March 1948) 73–76; M. Windholz Ed., *The Merck Index* , Rahway: Merck and Co., Inc., 1976, Misc–109; *ASHRAE Handbook of Fundamentals,*

American Society of Heating, Refrigerating, and Air Conditioning Engineers, Inc.

[31] There are, of course, chemicals so corrosive or toxic that gloves must be used, but they only feature in Appendix II of this book.

[32] I.e. by squirting out some of the contents of the syringe, held vertically – even if this procedure is much-honoured by the hospital staff in TV accident and emergency dramas. You are not concerned about avoiding embolisms.

[33] The volume of a drop is proportional to the radius of the tube and the surface tension of the liquid; it is inversely proportional to the density of the liquid. See Samuel Glasstone, *Textbook of Physical Chemistry*, London: Macmillan and Co., 2nd Edn. 1956, 489.

[34] This brings a new perspective to the concept of 'a graduate full of alcohol'.

[35] The identification of millilitres (ml) with cubic centimetres (cm^3) is now strictly exact.

[36] See, for example: D. A. Skoog, and D. M. West, *Fundamentals of Analytical Chemistry*, New York: Holt, Reinhart and Winston, 1976.

[37] Since the litre is not an approved unit of the SI system, the units here should strictly be written as moles/dm^3.

[38] Gordon Hutchings, *The Book of Pyro: pyrogallol; the PMK Formula*, Granite Bay CA: self-published 1991.

[39] This material has recently been changed by the Manufacturer and may soon be discontinued.

[40] Jack Fulton, in 'Waxed Paper Negatives', *The World Journal of Post-Factory Photography*, 4 (December 1999) 17.

[41] Mike Robinson, e-mail communication 14-11-97

[42] Liam Lawless, 'Enlarged Negatives by Reversal', *The World Journal of Post-Factory Photography*, 2 (October 1998) 41-4.

[43] The industry standard for image-handling computer software is Adobe Photoshop™.

[44] Dan Burkholder, *Making Digital Negatives for Contact Printing*, 2nd edn. Carrollton TX: Bladed Iris Press 1999.

[45] 360 dpi seems to be the concensus recommended by Burkholder and others. The human eye can usually resolve 7 lines/mm = 178 dpi, and at best 10 lines/mm = 254 dpi.

[46] Dan Burkholder's website:

http://www.danburkholder.com/

[47] HNO_3 69% w/w, D=1.41 g cm^{-3} ; molarity =15.4 M

[48] HCl 36% w/w; D=1.18 g cm^{-3}; molarity =11.6 M

[49] Fritz Ephraim, *Inorganic Chemistry*, (P.C.L. Thorne and E.R. Roberts, eds., London: Gurney and Jackson, 1948) 694.

[50] J.R. Partington, *A Text-book of Inorganic Chemistry*, 3rd Edn., London: Macmillan and Co, 1931, 591.

[51] R.C. Weast (ed.), *Handbook of Chemistry and Physics,* Florida: Chemical Rubber Company Press Inc, 1980, Table D-131.

[52] Now 10 g of gold is ca. 0.05 moles, so the volume of NO liberated from the complete dissolution of this will be 0.05 x 22.4 litres = 1.1 litres. There are ca. 28 litres in a cubic foot, so one can work out the level of NO_2 concentration in the atmosphere, given the room size and assuming complete mixing and no ventilation (!). In a large room of 10,000 cu.ft., the final NO_2 concentration resulting from the dissolution would be ca. 3 p.p.m. - to be compared with the Merck Index 'dangerous' level of 100 p.p.m. In a small room of 1000 cu.ft. the level would rise to 30 p.p.m. However this calculation is pretty non-significant because no-one is suggesting this should be done without adequate ventilation!

[53] Weast, *op cit*, Tables F-3, F-4

[54] The identification of millilitres (ml) with cubic centimetres (cm^3) is not strictly exact, but serves for most practical purposes.

[55] Though with the growth of digital imaging technology, this skill may become rare.

[56] R.C. Weast (ed.), *Handbook of Chemistry and Physics,* (Florida: Chemical Rubber Company Press Inc, 1980) Tables D-227 to D-276.

[57] M. Windholz (ed.), *The Merck Index* , Rahway: Merck and Co., Inc., 1976.

[58] Michael J. Ware, 'An Investigation of Platinum and Palladium Printing', *The Journal of Photographic Science*, **34**: 13 (1986) 165-177, and references cited therein. Michael J. Ware, 'Noble Metals for Common Images', in *Photochemistry and Polymeric Systems,* edited by J.M. Kelly, C.B. McArdle and M.J. de F. Maunder, Special Publication No. 125, Cambridge: Royal Society of Chemistry (1993) 252-265.

[59] These organic acids, originally referred to as 'vegetable acids' by Herschel, are all familiar 'household chemicals' - even the poisonous oxalic acid, which occurs (in small amounts) in the leaves of rhubarb, spinach, and sorrel.

[60] For more details of the chemistry of 'precious metal' printing see M. J. Ware, op. cit. 'Noble Metals for Common Images', ref. 57.

[61] Reference 4, 206.

[62] Sir J.F.W. Herschel, letter to H.F. Talbot, 31 March 1843; see *Selected Correspondence of William Henry Fox Talbot 1823-1874*, edited by Larry J. Schaaf, Science Museum and National Museum of Photography, Film & Television, (1994); see also Reference 4, 212.

[63] William Willis, British Patents, Nos. 2011 (June 1873), 2800 (July 1878), 1117 (March 1880). See also: Luis Nadeau, *History and Practice of Platinum Printing,* Atelier Luis Nadeau, Fredericton, (1984).

[64] Mike Ware, *Cyanotype: the history, science and art of photographic printing in Prussian blue*, London: Science Museum and National Museum of Photography, Film & Television 1999.

[65] Michael J. Ware, 'Photographic Printing in Colloidal Gold', *Journal of Photographic Science*, **42**:5 (1994) 157–161.

[66] E. Bordignon, L. Cattalini, G. Natile, and A. Scatturin, *Journal of the Chemical Society, Chemical Communications* (1973) 878.

[67] G. Natile, E. Bordignon, and L. Cattalini, *Inorganic Chemistry*, **15** (1976) 246.

[68] A.K. Al–Sa'ady, C.A. McAuliffe, R.V. Parish, and J.A. Sandbank, *Inorganic Syntheses*, **23** (1983).

[69] C.A. McAuliffe, R.V. Parish, and P.D. Randall, *Journal of the Chemical Society, Dalton Transactions*, (1979) 1730.

[70] A. Annibale, L. Canovese, L. Cattalini, and G. Natile, *Journal of the Chemical Society, Dalton Transactions,* (1980) 1017.

[71] Tanya Hughes and Michael J. Ware, *unpublished observations*, 1989.

[72] This appears not to be one specific compound or mixture, but is of variable composition, depending on the method of preparation. Prepared from gold chloride and aqueous ammonia, the explosive precipitate is largely (ClAuNH2)2NH, but on washing with ammonia hydrolysis to the more explosive (HOAuNH2)2NH occurs, and the equilibrium is reversed by washing with chloride.

[73] J.W. Mellor, *A comprehensive treatise on inorganic and theoretical chemistry*, 3 (1941) 582. See also *Bretherick's handbook of reactive chemical hazards*, 5th Edn. 1, 59.

[74] J. C. Roberts, *The Chemistry of Paper*, Cambridge: The Royal Society of Chemistry 1996

[75] Structurally more explicit – a cyclic molecule: –O–CH(CH_2OH)(CHOH)$_4$–

[76] α–cellulose is insoluble in 17.5% caustic soda; β– and γ– cellulose have shorter chains and are soluble in this reagent.

[77] Megan Gent and Jacqueline Rees, 'A conservation treatment to remove residual iron from platinum prints', *The Paper Conservator,* 18 (1994) 90–95.

[78] For introductory texts on photochemistry at the undergraduate level see: A. Cox and T. J. Kemp, *Introductory Photochemistry* (London: McGraw–Hill, 1971); R. P. Wayne, *Photochemistry*, (London: Butterworths, 1970). The comprehensive research manual is: J. G. Calvert and J. N. Pitts, Jr, *Photochemistry*, (New York: John Wiley & Sons Inc, 1966)

[79] The response of iron-based coatings (e.g. chrysotype, cyanotype or platino-palladiotype) is different intrinsically from that for photohardening of dichromated colloids (e.g. gum bichromate and carbon printing). There will even be differences between the various iron-based processes using different iron complexes.

[80] J. Baxendale and N.K. Bridge, *Journal of Physical Chemistry*, 59 (1955) 783; J.G. Calvert and J.N. Pitts, *Photochemistry*, (New York: John Wiley and Sons, 1967); C.G. Hatchard and C.A. Parker, *Proceedings of the Royal Society*, A235 (1956) 518.

[81] Michael J. Ware, 'An Investigation of Platinum and Palladium Printing', *The Journal of Photographic Science*, **34**: 13 (1986) 165-177.

[82] H.E. Spencer, *Journal of Physical Chemistry*, 73 (1969) 2316.

[83] H.E. Spencer and M.W. Schmidt, *Journal of Physical Chemistry*, 75 (1971) 2986.

[84] R. Livingston, *Journal of Physical Chemistry*, 44 (1940) 601.

[85] The internal filter effect is substantially absent in iron-silver sensitizers, and gold(I).

[86] Properly, in a heterogeneous system, the optical density should be calculated using the Koubelka-Munk theory, which takes account of significant scattering. However the present approximation will serve for an 'order-of-magnitude' calculation.

[87] See Captain Abney, *Instruction in Photography*, (7th edn. London: Piper and Carter 1886) 268. Peak response is shown near the Fraunhofer G line at 434 nm

[88] Rigorously, the yield should be calculated by integrating over the whole waveband of actinic light, to take account of the variations of *I, f, and* ϕ with wavelength λ. The present approximation will serve for most purposes, however.

[89] The intrinsic printing exposure scale of the iron-based sensitizers generally appears to be 7 or 8 stops, corresponding to arithmetic factors of $2^7 = 128$, to $2^8 = 256$.